THE USE OF GLUCOSE AS ECOLOGICAL REDUCING AGENT FOR SULPHUR DYES: OPTIMIZATION OF EXPERIMENTAL CONDITIONS

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Abstract

At the present time, dyeing of textile material requires the use of various auxiliaries. These used agents have adverse effects on the environment. In general, for the dyeing with sulphur dyes, a reducing agent is used to transform the dye molecule to a water soluble leuco form that can diffuse into the fibre. In this study, three reducing agents were used : the sodium sulphide, sodium dithionite and glucose as an environmentally friendly reducer. To compare their effect on the reduction of the sullphur dyestuff, the redox potential, pH and the colour yield (K/S) were measured according to the concentration of reducing agent and caustic soda concentration. Results of leuco sulphur black B reduction by the different reducing agents were evaluated by measuring the colour yield (K/S) and the brightness variation after the washing process. The obtained results showed that glucose can offer some scientifically results similar to those done with sodium sulphide which can give for the reduction of sulphur dyestuff

Keywords: Sulphur dye, Dyeing, Reduction, Reducing Agent, Glucose

Introduction

Cellulosic substrates especially cotton, rayon, and paper, are very hydrophilic and, therefore, require hydrophilic soluble dyes for their coloration from a dye bath. Current dyes designed for cellulosic polymers are direct, vat, sulfur, and reactive dyes. Sulphur dyes are one of the less costs of all dye classes used on cellulosic fibres and their blends (Senior & Clarke, 1986). In fact, this dye category was widely used to produce inexpensive, medium to heavy depths. In its application, sulphur dye requires a complicated procedure (reduction and oxidization mechanism). Reduction of sulfur dye macromolecular under alkaline conditions affects the di- or polysulfide bonds in the dye and generates the thiol form of the dye having a high affinity to cellulosic fibers. After dye diffusion, the leuco-soluble form can be converted back to its water-insoluble form in situ in the fibres by oxidization to generate the final colour (Zollinger, 1987).

The most used reducing agent in industrial scale has been the sodium sulphide (Na_2S) and sodium hydrogen sulphide (NaHS) due to their efficiency and their weak cost. However, the sodium dithionate ($Na_2S_2O_4$) combined with caustic soda was the most widely used in reduction of vat dye. The dithionite is not industrially used for sulphur dye due to its difficult to control. Sodium dithionite destroy some number of sulfur dyes by over-reduction (Heid et al., 2004) and it can’t be recycled from the wastewaters and used again in the reduction process (Bechtold et al., 1992). Moreover, it is very easily oxidized by atmospheric oxygen (Camacho et al., 1997). The generation of sulfate, sulfite and thio-sulfate ions have harmful effect on the environment due to their toxicity as well as their corrosive effect on the wastewater treatment. In addition, sodium dithionite affects the microorganism processes in the wastewaters treatment and a toxic hydrogen sulfide can be generated from the sulfate present in the wastewaters (Bozic & Kokol, 2008; Kulandainathan et al., 2007).

The most inconvenience of these reducing agents was their dangerous effects on the environment due to the toxicity of the hydrogen sulphide and the corrosion effect on effluent drainage system. In fact, in order to protect the environment, such as the maintaining of the water purity, the reducing agents containing sulfide are excluded.

In this case, from an environmental point of view, the use of glucose and others sugars as reducing agents were very promising alternative. However the reduction of sulphur dye with D-sugars has been reported (Blacburn & Harvey, 2004). Then, the redox potential of various hexose and pentose mono-saccharides and reducing disaccharides was recorded and compared. Unfortunatetly, these reducing agents reduce sulphur dye at high temperatures, and their optimum colour yield is reached only above 90°C (Senor, 1995, Bechtold et al., 2004). Moreover, they cannot reduce all dyes and their major inconvenience is the loose of their reducing power due to their decomposition into intermediate products.

In this paper, the stability of the sodium sulphide, sodium dithionite and glucose as reducing agent for sulphur dyes in dyebath was investigated. Then, their optimum conditions parameters were carried out in order to study the efficiency of glucose to reduce the sulphur dye.

Materials and Methods

Commercially bleached and unfinished cotton with the specifications cited in table 1 supplied by SITEX, Tunisia.

Table 1. Characteristic of woven fbric

Weave weight ($g.m^{-2}$)	Yarn count (picks/cm)		Yarn density	
	warp	weft	warp	weft
238	14	11	11.5	12.5

The used Leuco sulfur dye Black B (BEZEMA AG Switzerland)

The fabric passes in open width through a ‘nip’. The nip is the padding mangle, in which heavy rollers pressed closely together along their length, and are rotated in opposite directions to carry the fabric through and the system at a constant speed. Then the fabric is thoroughly rinsed and, exposed to the atmosphere or it passes through a bath of oxidization, where oxidization generates the mechanically entrapped insoluble pigment.

The dyeing quality was evaluated using a colour parameter (K/S). So the reflectance of the dyed samples was measured at 660nm on SpectroFlash SF600 spectrophotometer with dataMaster2.3 software (Datacolor International, USA). Then the colour yield was determined according to the Kubelka-Munk equation. Then the CIE L* a* b* measurements of the dyed fabric were carried out on SpectroFlash SF 600 spectrocolorimeter.

The redox potential was measured using an oxidation-reduction potential platinum electrode

connected to a pH meter (potentiometer, Tacussel LPH 230 T) and recorded in mV. Each test was repeated three times.

Results and discussion

Stability of reducing agents

In this part the main properties of used reducing agent during dyeing process was investigated to know their stability in the dyeing bath. Indeed, to analyze the stability of these agents in the time, the potential in solution was measured to intervals of 10 minutes at fixed temperature. The experimental results are shown in Figure.1.

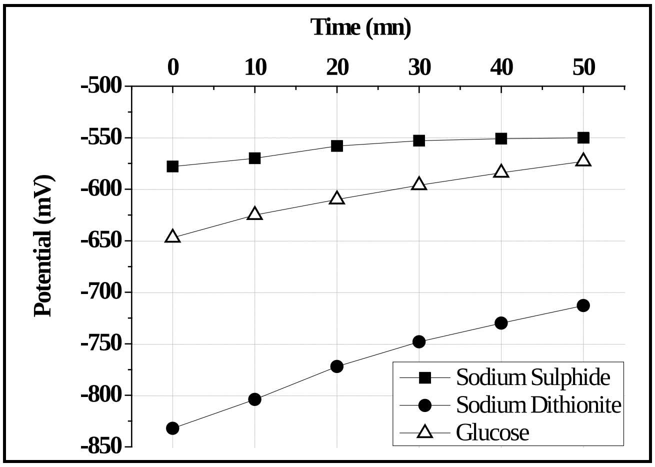

Figure 1. Evolution of redox potential as a function of dyeing time

The reduction potential varies in a distinct manner between the three reducing agents. In fact, the sodium dithionite shows the most variation of redox potential, it is between -834 mV and -713.mV. Whereas sodium sulphide has a variation of -28 mV during the time. Generally, the reducing agent presenting the lowest variation of the redox potential is the most stable during dyeing processes. Therefore, we can classify the three reducing agents by order of increasing stability as follows: Sodium dithionite < Glucose < Sodium sulphide.

Then, to evaluate the influence of the temperature on the reduction potential for used reducing agents, measurements were carried out at five temperature value; 60°C, 70°C, 80°C, 90°C and 100°C, in which their results are mentioned in Figure 2.

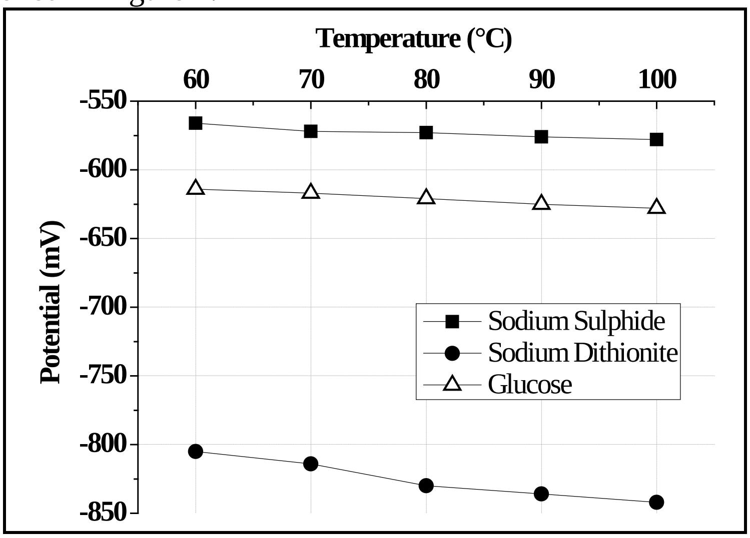

Figure 2. Evolution of redox potential as a function of dyeing bath temperature

In fact, it can be seen that for the sodium sulphide, the variation of redox potential is between -566 mV and -578 for a variation of 40°C, it is between -614 mV and -628 mV. Contrarily for the sodium dithionite, the action of temperature was very important on the redox potential, so it presents a variation of -37 mV. It can be explained that the reducing agent loses its reducing power in long time and, as increasing temperature, its reactivity increases what generates an increment of the potential. The obtained results demonstrate the same classification of stability according to the temperature as in the time; sodium dithionite < glucose < sodium sulphide.

Effect of reducing agent concentration

The dyeing of textile material with insoluble dye requires two steps. The reduction of dye into leuco soluble form and it's oxidization in second step. The best reducing agent is whose permits to maintain the dye in its leuco-soluble form throughout dyeing. an appropriate amount of reducing agent is vital since an insufficient quantity results in off shades and will lower the overall fastness of dyeings. Results mentionned in Figure 3 show that the higher colour yield was obtained at a concentration of 6 $g.L^{-1}$ for sodium dithionite and glucose and at 7 $g.L^{-1}$ for sodium sulphide. For different reducing agent, the colour yield was inproved with the increasing of concentration of reducers. The better one is of the sodium dithionite, this result confirm the important reducing power of the sodium dithionite. Then the same behaviour was obtained for the sodium sulphide and the glucose as reducing agents. The influence of reducing agent concentration is related to the pH value of the dyeing bath. These results were confirmed by the variation of the redox potential mentioned in the table 1. In fact, the redox potential vary slowly with the variation of the reducing agent concentration. Firstly, the redox potential increases to reaches the maximum value, then it decreases where the optimum reducing agent concentration was obtained.

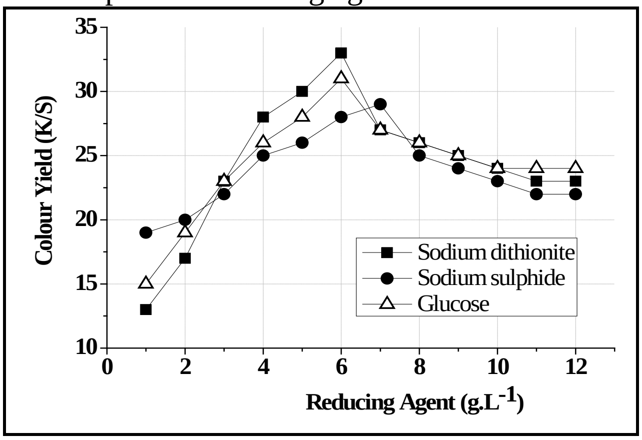

Figure 3. Effect of reducing agent concentration on colour yield (K/S)

Table 1. Variation of pH and Redox Potential as function of Reducing agent concentration

Reducing agent (g.L^{-1})	Sodium Dithionite		Sodium Sulphide		Glucose	
	pH	Redox Potential (mV)	pH	Redox Potential (mV)	pH	Redox Potential (mV)
1	11,63	-796	12,02	-550	11,34	-580
2	11,71	-812	12,09	-552	11,43	-606
3	11,86	-820	12,11	-574	11,62	-616
4	11,97	-826	12,17	-578	11,83	-620
5	12,02	-836	12,04	-556	12,01	-612
6	11,96	-838	12,13	-558	12,17	-618
7	11,88	-830	12,27	-558	12,26	-622
8	11,83	-834	12,39	-554	12,35	-625
9	11,72	-832	12,47	-557	12,42	-626
10	11,7	-836	12,53	-555	12,49	-623
11	11,64	-832	12,59	-552	12,53	-628
12	11,6	-838	12,63	-553	12,55	-623

Effect of caustic soda concentration

First, it is well known that pH of dye bath affects considerably sulfur dyeing and especially the reduction of the dye while dyeing cotton fiber. In order to study the influence of caustic soda on the reduction of sulphur dye, dyeings were realized at optimal reducing agent concentration. All results are showed in Figure 4. It is clearly that the caustic soda concentration led to an increase of pH for the three used reducing agents. The small increase is the one of the sodium sulphide, contrarily to sodium dithionite where it shows an important variation. For sodium dithionite, the reducing agent loses its reducing effect by contact with air. Since to work safe from air require a high-level equipment, what is not always envisageable in industry. During dyeing processes, the sodium dithionite as oxidizing consumes sodium hydroxide, because the sulfinate ion (SO_2^{2-}), which is responsible for the dye reduction is obtained according to the following reaction :

$$Na_2S_2O_4 + 2NaOH \longrightarrow Na_2SO_3 + Na_2SO_2 + H_2O$$

After reaches the optimum, the pH decreases which explained by the consumption of the caustic soda.

For the sodium sulphide, the incrasing of the pH value can be explained by the reaction of the reducing agent with the water, where it generate the formation of the caustic soda according to the following equation :

$$Na_2S + H_2O \longrightarrow NaOH + NaHS$$

For the glucose, the reduction of the molecule under alkaline conditions provides some products which are responsible to the increasing of the pH value.

After optimizing the concentration of the reducing agent in the dye bath for the three used reducing agents, it is necessary to quantify the optimum of the caustic soda concentration. The variation of the redox potential as function of caustic soda concentration show that the redox potential is nearly stable at -836 mV for sodium dithionite, at - 620 mV for glucose and at -555 mV for sodium sulphide. These results explain the variation of the colour yield demonstrated in Figure 5. the sodium dithionite presents the important reducing power so the higher colour yield. The adequate caustic soda concentration is 15 $g.L^{-1}$ for the sodium sulphide and the glucose and 20 $g.L^{-1}$ for sodium dithionite. Beyond these concentration, the colour yield decreases.

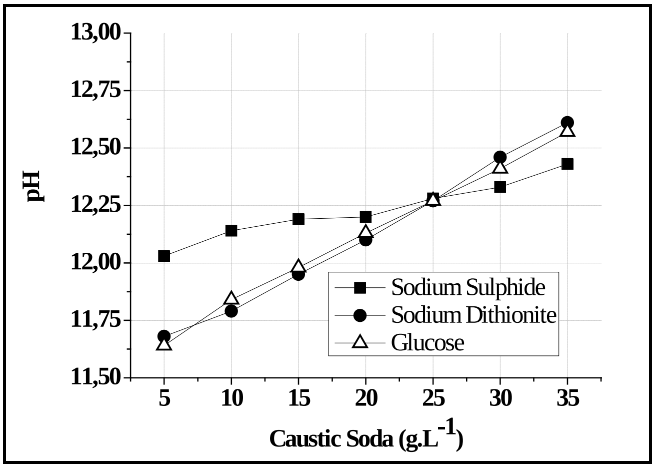

Figure 4. Effect of Caustic soda concentration on pH

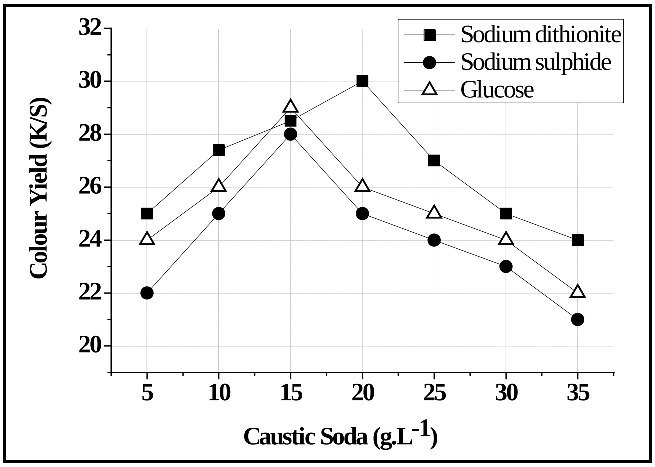

Figure 5. Effect of Caustic soda concentration on colour yield (K/S)

Variation of the Brightness

The experimental results representing the effect of the reducing agent and the washing process on the evolution of the fabric brightness are shown in table 2. For which used reducing agent, more the temperature increases more L* decreases, which means that the increment of temperature encourages the fixing of the dye on the cotton fabric. It can be explained that increasing temperature leads to increase the solubility of the dye (that means an important reduction rate) what limits the formation of aggregation. But, it is not necessary to use an important thermal agitation in order to avoid the risk of succeeding to an inverse phenomenon.

Table 2. Effect of Reducing agent and Temperature on brightness variation

		Temperature				
Reducing Agent		**60**	**70**	**80**	**90**	**100**
Sodium Sulphide	**L*without washing**	**43,4**	**40,8**	**39,8**	**39,01**	**37,5**
	L* after washing	**57,97**	**56,79**	**54,19**	**53,83**	**54,3**
	ΔL*	**14,57**	**15,99**	**14,39**	**14,82**	**16,8**
Sodium Dithionite	**L*without washing**	**41,3**	**39,8**	**39,8**	**39,4**	**38,6**
	L* after washing	**62,58**	**61,12**	**56,52**	**54,74**	**57,7**
	ΔL*	**21,28**	**21,32**	**16,72**	**15,34**	**19,1**
Glucose	**L*without washing**	**40,08**	**40,04**	**39,5**	**39,47**	**37,2**
	L* after washing	**57,62**	**57,43**	**55,84**	**54,88**	**58,8**
	ΔL*	**17,54**	**17,39**	**16,34**	**15,41**	**21,6**

Results show that after only one washing process, the dyeing at 90 °C has the small rate of dye destruction and the sodium sulphide possesses the weakest variation of the brightness which proves its stability in the dye bath. Then the dyeing with the sodium dithionite presents an important fall of the brightness. It is probably due to the weak fixing rate of the sulphur dye which can be explained that while increasing temperature, the energy of reduction reaction will be raised. As well as in presence of sodium dithionite, very powerful reducing agent, the reaction will be achieved brutally. Besides that the sodium dithionite, in contact with air by decomposition, produces an acid which easily neutralized by the alkali in the dye bath. Therefore, a loss of the rate of reduced dye and aggregations forms on the cotton fabric was observed, which can be easily eliminated with a simple washing.

In the same case, the variation of brightness as function of reducing agent shows that the best results were obtained with the sodium sulphide, secondly the glucose and sodium dithionite in third class. This observation confirms the classification of the three reducing agents.

Study of the Mixture of dyestuff

After optimizing different optimum concentration of used auxiliaies, these experimental conditions were used to reduce a mixture of two sulphur dyes. The main idea of this part is to study the variation of redox potential of two leuco sulphur dyes in the same dye bath. The proportions of used dyes in the mixture are 30% Black B and 70% of other leuco sulphur dye (Yellow MS, Green BGS, Red 2BN and the Brown GFL)

The measures show that the pH presents the same behaviour when the sodium sulphide and the glucose were used as reducing agent with the different mixtures. Contrarily, for the sodium dithionite, the pH behaves in a different manner as obtained for the one of the leuco Black B. Concerning the redox potential as shown in the table 3, two categories of behaviour were observed. First, the redox potential is the same of the major constitution of the dye bath (the case of Black B – Green BGS where the redox potential of the mixture is the one of Green BGS and the same case for the Black B – Brown GFL). The behaviour of these two mixture is the same for three used reducing agent what poves the same chemical composition of suphur leuco Green BGS and Brown GFL. Second, for other mixture, the redox potential shows a synergy between two used leuco sulphur dyes (the redox potential of Black B – Yellow MS is – 678 mV with the glucose as reducing agent and – 671 mV for the Black B – Red 2BN for the same reducing agent).

Table 3. Effect of Reducing agent on Redox potential of Mixture of sulphur dyes

Sulphur dye	Sodium Sulphide	Sodium Dithionite	Glucose
Black B	-570	-834	-632
Yellow MS	-603	-802	-594
Black B - Yellow MS	-578	-818	-678
Black B	-570	-834	-632
Green BGS	-588	-824	-681
Black B - Green BGS	-588	-824	-681
Black B	-570	-834	-632
Red 2BN	-585	-794	-630
Black B - Red 2BN	-590	-823	-671
Black B	-570	-834	-632
Brown GFL	-592	-814	-682
Black B - Brown GFL	-592	-814	-682

This study of redox potential of sulphur dye in mixture confirms that the sodium sulphide and the glucose behave in the same manner in the dye bath. Some leuco sulphur dye possess the same behaviour and priori the same chemical structures.

Conclusion

In first time, the aim of this work is to study the optimization of some dyeing parameters (type of reducing agent and its concentration, caustic soda, effect of the temperature). Then the possibility of use of environmentally friendly system as the glucose as reducing agent for leuco sulphur dye was investigated. It has been showed that the sodium sulphide and the glucose provides best results of sulphur dye reduction and the less brightness variation according to the washing processes. Therefore, the sodium dithionite possess the important reducing agent power but it's main inconvience is the instability in the dye bath. Finally, the obtained results using glucose as reducing agent was similar to those obtained with sodium sulphide. In fact, it is possible to replace the toxic reducing agents (sodium dithionite and sodium sulphide) by the ecological product as the glucose in the reduction process of sulphur dye.

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