

Use of glucose as an ecofriendly reducing sugar in the application of sulphur dyes —Comparative study with traditional reducing agent

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Attempts have been made to replace the mostly used reducing agent (sodium sulphide), and the most effective reducing agent (sodium dithionite), with an environment- friendly reducing sugar (glucose). This comparison is based on the redox potential and *pH* used under different concentrations of reducing agent, caustic soda and sodium carbonate. The dyeing performance resulting from the reduction of the CI Leuco Sulphur dye Black 1 by each one of the studied reducing agents is appreciated by measuring the colour yield and by evaluating dyeing fastness. The obtained results show that glucose can offer an environmentally safe alternative to sodium dithionite and sodium sulphide as a reducing agent in sulphur dyeing processes.

Keywords: Cotton, Dyeing, Fastness property, Glucose, Leuco sulphur dye, Reducing sugar

1 Introduction

Sulphur dyes are one of the most popular dye classes used on cellulosic fibres and their blends^{1, 2}. Sulphur dyes are widely used to produce economical black, blue, brown and green shades on cellulosic fibres in medium to heavy depth. However, sulphur dyes require a complicated application procedure (reduction and oxidation mechanism) because they are practically insoluble in water and have no affinity for cellulosic fibres in such a state. Thus, these dyes have to be reduced before dyeing to be converted into the water soluble form which has substantivity towards fibres. After absorption into the fibres to be dyed, this dye should be reoxidised to the original water insoluble dye pigment form *in situ* in the fibres³⁻⁵. Commonly used oxidising agents are hydrogen peroxide or atmospheric oxygen under harsh conditions (high *pH* or temperature).

The most widely used traditional reducing agents are sodium sulphide (Na₂S) and sodium hydrogen sulphide (NaHS). Technically, these are still most widely preferred, not only for their efficacy but also because they are relatively inexpensive. Nowadays, however, these are increasingly subject to scrutiny on environmental grounds. The environmental problems arising from sulphides include the toxicity of

hydrogen sulphide, corrosion of the effluent drainage system, damage to the treatment works and the often associated high *pH* and unpleasant odours⁶.

Several reducing agents have been suggested as environmentally more acceptable alternatives to the alkali sulphides. All of them are more expensive and exhibit other disadvantages^{7,8}. For example, the reduction may be more difficult to control, or a particular agent may be effective only with a limited range of dyes. Moreover, the alternatives are found to be less effective than the alkali sulphides in terms of colour yield. The fact that such compounds do not generate hydrogen sulphide is also not a guarantee from environmental problems, for example, some give quite high COD levels. The most obvious alternative is sodium dithionite (Na₂S₂O₄) with alkali, the reducing agent most widely used with vat dyes. On dyeing with sulphur dyes, however, the process is difficult to control and some dyes may be partly destroyed by over reduction. Nevertheless, dithionite is effective with CI solubilised sulphur and sulphurised vat dyes. Sodium hydroxide is the alkali used in conjunction with dithionite. Sodium carbonate is a possible alternative when CI solubilised sulphur dyes are used but it is insufficiently alkaline for the CI sulphur brands, requiring careful control if over reduction and the associated lower yields are to be avoided⁹. However, the disadvantage of sodium dithionite is that it has a low stability; it is very easily

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oxidized by atmospheric oxygen¹⁰. Moreover, the stability of its alkaline solutions reduces with the increase of temperature even in the absence of oxygen. So, large amounts of dithionite and sodium hydroxide are needed over the stoichiometric requirements of the reduction process. On the other hand, the oxidation of byproducts causes various problems with the disposal of wastewaters. The generation of sulphate, sulphite and thiosulphate ions shows harmful effects on the environment due to their toxicity as well as their corrosive effects on the waste lines.

The most promising alternative to sulphides, from an environmental point of view, is the use of the reducing sugar glucose with sodium hydroxide or sodium carbonate. This system does not satisfactorily reduce all dyes. It is reasonably effective with CI solubilised sulphur brands^{7,11} with which it may be used either as the sole reducing agent or in conjunction with sodium polysulphides, usually resulting in increased dye yields. It can be used as an additional reducing agent with CI leuco sulphur dyes, thus giving lower sulphide content in the dye bath, or together with sulphide or polysulphide in the reduction of the traditional water insoluble CI sulphur brands¹¹. The versatility of glucose-based binary systems has been emphasised¹². The major problem with an alkaline glucose system is that it is gradually transformed into various decomposition products, thus losing its reducing action. The intermediate byproducts possess some reducing action but are not sufficiently stable.

Although the reduction of sulphur dye with D-sugars has already been reported¹³, there is still further fundamental and applied research needed to reach successful concrete application of this reducing agent on the industrial scale. In this investigation, a comparative study between sodium dithionite, a standard commercial sulphide-based reducing system and reducing sugar glucose has been carried out in order to assess the possibility of their use as ecofriendly alternatives in the reduction of sulphur dyes.

2 Materials and Methods

2.1 Materials

The commercially bleached and unfinished 100% cotton fabric, having the specifications plain weave, weight 242 g/m², ends/cm 16, picks/cm 12, warp count 12.5 and warp count 12, was used. A commercial sample of CI Leuco sulphur dye Black 1, three different reducing agents (sodium dithionite, sodium sulphide and glucose), wetting agent (Albaflow Pad) and sequestering agent (Trilon TB)

were procured from Clariant. Caustic soda and sodium carbonate, both of general laboratory grade, were supplied by Sigma Aldrich Company.

2.2 Redox Potential Measurement

The redox potential was measured using an oxidation-reduction potential platinum electrode connected to a pH meter (Cyberscan pHmeter 1500- Eutech Instruments) and recorded in mV.

2.3 Dyeing Process

Dyeing was carried out using a dyeing machine. Five grams pieces of fabric were dyed at a liquor ratio of 20:1, using stainless steel dye pots, each of 250 cm³ capacity. Schematic procedure of dyeing is shown in Fig.1. At the end of dyeing, the samples were rinsed for 5 min in hot water (60°) followed by rinsing in cold water for 5 min and then oxidised at an ambient air. At the end of oxidation, the samples were rinsed in running cold water for 5 min and allowed to dry in open air.

2.4 Dyeing Quality Evaluation

The dyeing quality was evaluated using a colour yield parameter (K/S). The reflectance of the dyed samples was measured at 660nm on SpectroFlash SF600 spectrophotometer with dataMaster2.3 software (Datacolor International, USA). The colour yield was determined according to the Kubelka-Munk equation.

2.5 Fastness Testing

The dyed samples were tested for fastness properties according to standard methods, such as for colour fastness to washing ISO 105-C02:1989, colour fastness to rubbing ISO 105- X12:1987, and colour fastness to light ISO 105-B02:1988 (carbon arc)¹⁴.

3 Results and Discussion

3.1 Stability of Reducing Agents

In order to verify the stability of different reducing agents with time, measurements of redox potential have been realized during the dyeing process. The experimental results are shown in Fig.2.

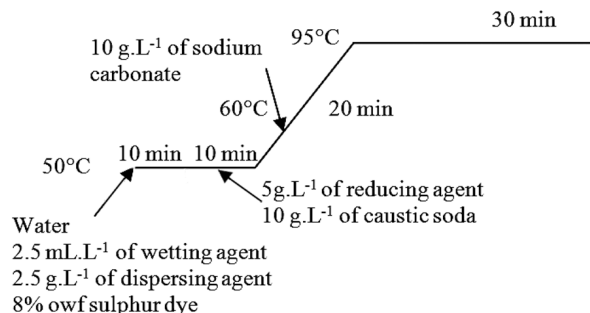


Fig.1— Schematic diagram of dyeing procedure

The downfall of reduction potential varies, with time, in a distinct manner, among the three reducing agents. In fact, it is between -832 mV and -703 mV for sodium dithionite, between -647 and -569 mV for glucose and between -578 and -548 V for sodium sulphide. The reducing agent, whose potential decrease is the lowest one, would be the most stable during dyeing. Thus, we can classify the three reducing agents by order of increasing stability and decreasing reducing power as sodium dithionite < glucose < sodium sulphide.

To study the influence of temperature of the dyeing bath on the reduction potential of each reducing agent, these parameter measurements were carried out at temperatures between 85°C and 100°C and at the gradient of rise in temperature. Each measurement was repeated three times. The reducing power was improved slightly as a function of the temperature for sodium sulphide and glucose. In the case of sodium dithionite, the potential increase is more pronounced. Temperature has the same influence as the dyeing time on the stability of the three reducing agents and shows the same order as shown previously: sodium dithionite < glucose < sodium sulphide.

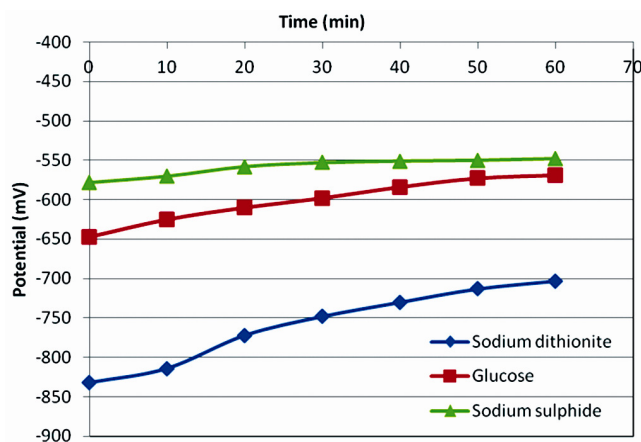


Fig. 2— Evolution of redox potential as a function of dyeing time for the different reducing agent

3.2 Effect of Reducing Agent Concentration

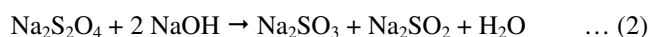
In the context of the traditional application of sulphur dyes to cellulosic fibres, for optimum results, a successful reducing agent should maintain the dye in its reduced form throughout the dyeing. An appropriate amount of reducing agent is vital since an insufficient quantity results in off shades and will lower the overall fastness of dyeings, whereas an abundance of reducing agent can over reduce the dyes¹⁵. In addition to that required to reduce the dye, a proportion of the reducing agent will be oxidised by air; hence, the reducing agent has to satisfy several criteria in order to be employed successfully in sulphur dyeing.

Table 1 shows that the redox potential does not vary significantly for the different concentrations of reducing agent. It gradually increases until it reaches a maximum value beyond which it decreases as a function of reducing agent concentration.

The *pH* value increases according to the concentration of the reducing agent, irrespective of its nature, except for sodium dithionite where it reaches a maximum value at a concentration of 5g.L⁻¹, beyond which it decreases. Indeed, in the case of sodium sulphide, it reacts during dyeing with water, forming caustic soda according to the following reaction, and this can explain the increase of *pH* values



For glucose, the intermediate byproducts obtained during its reduction in alkaline conditions, can eventually be responsible for the *pH* increase. However, in the case of sodium dithionite, oxidation during dyeing is accompanied by the consumption of sodium hydroxide according to the following reaction:



This reaction allows the formation of the sulfinate ion (SO₂⁻) which is responsible of the dye reduction,

Table 1 — Effect of reducing agent concentration on *pH* and redox potential

Reducing agent concentration, g.L ⁻¹	Sodium dithionite		Glucose		Sodium sulphide	
	<i>pH</i>	Redox potential, mV	<i>pH</i>	Redox potential, mV	<i>pH</i>	Redox potential, mV
1	11.78	-805	11.40	-614	12.09	-550
2	11.73	-814	11.47	-617	12.12	-550
3	12	-830	11.70	-621	12.17	-578
4	12.13	-836	11.69	-625	11.99	-570
5	12.03	-837	12.00	-629	12.00	-558
6	11.92	-836	12.16	-627	12.12	-559
7	11.87	-835	12.31	-626	12.29	-557
8	11.74	-834	12.46	-625	12.43	-555

and causes, beyond a certain concentration of the reducing agent (5g.L^{-1}), the gradual decrease in pH due to the consumption of NaOH .

Figure 3 shows that the colour yield improves with the reducing agent concentration to a certain value beyond which it deteriorates. This is due to the over reduction of sulphur dye by these reducing agents under these conditions. The higher colour yield is obtained at a concentration of 5g.L^{-1} for sodium dithionite and glucose and at 6g.L^{-1} for sodium sulphide, which implies that the increased dye reduction and, therefore, higher dye exhaustion has occurred. Besides, at these conditions, it can be observed that the use of sodium dithionite in reduction shows better colour yield than that obtained when reduction is realized using glucose; which, in turn, gives better coloristic performance in comparison to sodium sulphide.

3.3 Effect of Caustic Soda Concentration

In order to improve the performances of the reducing agents at their optimal concentration (5g.L^{-1} for sodium dithionite and glucose and at 6g.L^{-1} for sodium sulphide), dyeings were realized with different concentrations of caustic soda ($5\text{-}50\text{g.L}^{-1}$). Figure 4 (a) shows that the increase in caustic soda concentration leads to an increase in pH from about 11.63 to 12.85 for sodium dithionite, from about 11.65 to 12.69 for glucose; and from 12.00 to 12.55 for sodium sulphide.

At different caustic soda concentrations, the redox potential remains stable at -862 for sodium dithionite, at -631 for glucose and at -517 for sodium sulphide. This also explains the results achieved in Fig.4 (b) In fact, the reducing agent with the highest reducing power is the one that has the best colour strength which is the case of sodium dithionite, followed by glucose and then sodium

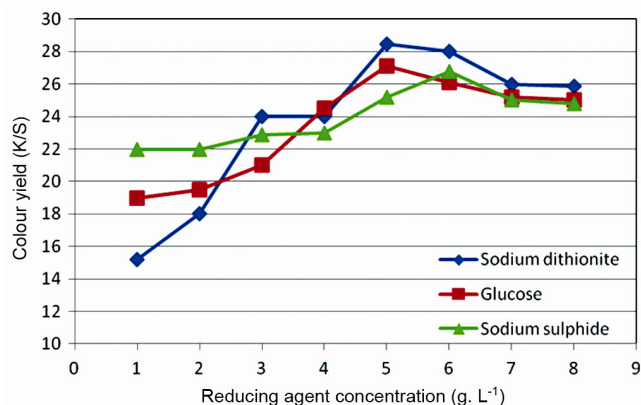


Fig.3— Effect of Reducing agent concentration on colour yield (K/S)

sulphide. Optimum colour yield is obtained at a caustic soda concentration of 20g.L^{-1} using sodium dithionite as a reducing agent and at 15g.L^{-1} using sodium sulphide or glucose to reduce the sulphur dye.

Beyond these optimal concentrations of caustic soda, the colour yield decreases irrespective of the reducing agent used. High alkalinity does not give a high and stable colour yield without risks of over reduction, irrespective of reducing agent nature.

3.4 Effect of Sodium Carbonate Concentration

After optimizing the concentrations of the three reducing agents and sodium hydroxide in the dye bath, it is particularly relevant to determine the concentration of sodium carbonate to achieve the best dye exhaustion. Dyeings were realized with different concentrations of sodium carbonate ($5\text{-}50\text{g.L}^{-1}$) using the three reducing agents and caustic soda at their optimum concentrations (sodium dithionite 5g.L^{-1} and NaOH 20g.L^{-1} ; glucose 5g.L^{-1} and NaOH 15g.L^{-1} and sodium sulphide 6g.L^{-1} and NaOH 15g.L^{-1}).

Figure 5 (a) shows that with the increase in sodium carbonate concentration, the alkalinity of dyeing bath increases consequently. The pH value varies significantly for sodium dithionite and sodium

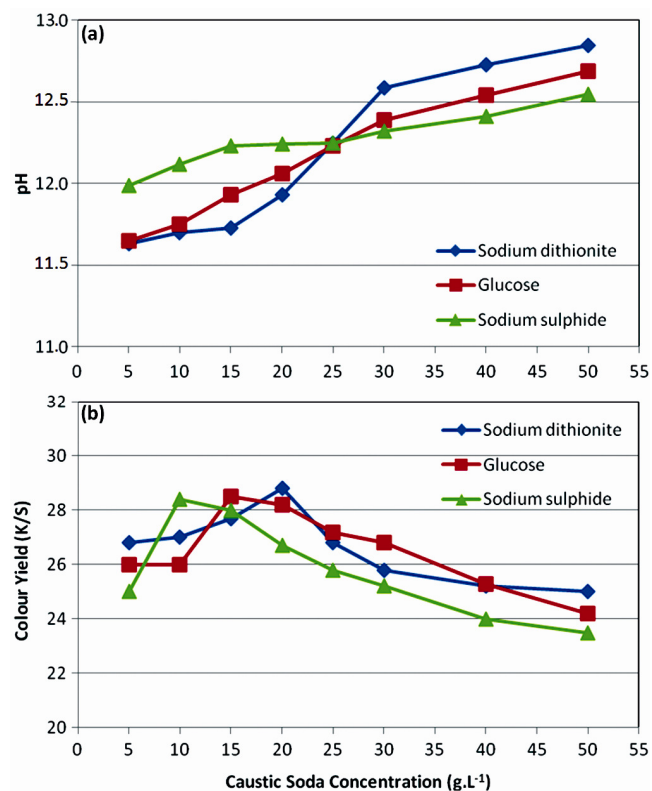


Fig.4— Effect of Caustic Soda concentration on (a) pH and (b) colour yield

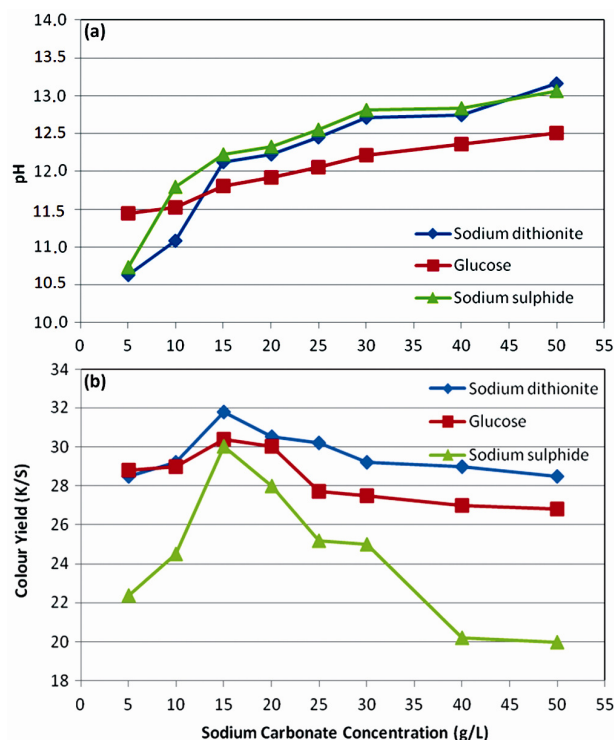


Fig.5— Effect of Sodium Carbonate concentration on (a) pH and (b) colour yield

sulphide from 10.63 to 13.16 and from about 10.73 to 13.06 respectively. The variation in pH in the case of glucose is less important (11.45 - 12.51).

At different sodium carbonate concentrations, the redox potential remains stable at -852 for sodium dithionite, at -631 for glucose and at -525 for sodium sulphide. Sodium carbonate is used to prepare the textile substrate and to favour a certain degree of textile support swelling during the dyeing process approving the dye diffusion. By optimizing the concentration of sodium carbonate (15g.L^{-1}), colour exhaustion improves for the three reducing agents [Fig.5 (b)]. At a higher concentration, colour yield decreases (significantly in the case of sodium sulphide), reflecting over reduction.

The obtained results show that at the optimal conditions in terms of reducing agent, caustic soda and sodium carbonate concentrations, the best colour yield is obtained using sodium dithionite to reduce the sulphur dye. Glucose and sodium sulphide give comparable colour exhaustion which is slightly better for glucose.

3.5 Fastness Testing

Table 2 shows that the rub fastness and the light fastness of dyeings realized at the optimal conditions in terms of reducing agent, caustic soda and sodium

Table 2 — Fastness of dyeing obtained at the optimum conditions

Reducing agent	Wash fastness		Rub fastness		Light fastness
	60°C	90°C	Dry	Wet	
Sodium dithionite	5	4-5	4-5	4	6
Glucose	4-5	4	4-5	4	6
Sodium sulphide	4-5	4	4-5	4	6

carbonate concentrations, as well as the kind of reducing agent used, are good. Wash fastness values at 60°C and 90°C of dyeings realized with sodium dithionite are better than those realized with sodium sulphide or glucose as reducing agent.

4 Conclusion

Glucose can be used as a green reducing agent for CI Leuco sulphur dye Black 1 replacing the mostly used reducing agent due to its stability. But it is not the most effective one as compared to sodium sulphide and cannot substitute the more efficient but less stable reducing agent sodium dithionite. Indeed, by optimizing some dyeing parameters (reducing agent, caustic soda and sodium carbonate concentrations), it is observed that the glucose is able to give shades slightly less intense and less resistant to washing than that obtained with sodium dithionite and comparable to those obtained using sodium sulphide as a reducing agent.

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