

Dyeing of cotton with vat dyes using alkaline catalase alongwith iron(II) salt

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Received 2 January 2019; revised received and accepted 14 August 2019

In this study, attempts have been made to replace sodium hydrosulphite with alkaline catalase in combination with iron (II) salt for dyeing cotton with vat dyes. The results show that alkaline catalase with iron (II) salt is quiet effective and capable of substituting sodium hydrosulphite with comparable dye strength and colour fastness. While reduction potential values of dyebaths are found to be almost same in both hydrosulphite and alkaline catalase along with iron(II) salt systems, the stability of the baths in absence and presence of dye is found superior in the new reduction system as compared to those in hydrosulphite system. Dye strength results show mixed findings, i.e. for some dyes, dye strength is higher in new reduction system, while for rest of the dyes, it is higher in hydrosulphite system.

Keywords: Alkaline catalase, Cotton, Dye strength, Hydrosulphite, Iron (II) salt, Vat dye

1 Introduction

Amongst the cellulose polymeric varieties, cotton is considered as one of the important textile fibres^{1,2}. A number of major dye classes are used for coloration of cellulose, including reactive, vat, sulphur, direct, azoic, solubilized vat dye, etc. The choice of dye depends on the required shade, its fastness and cost³. Vat dye is the most popular among dye classes used for coloration of cotton, particularly when high fastness colour standards are to be met⁴.

Vat dyes are insoluble in water and are converted into water soluble form called leuco dye by reduction with a strong reducing agent, like sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$) and solubilising agent sodium hydroxide (NaOH); in this state the dye shows affinity for cotton⁵. The reduced dyestuff diffuses inside fibre and gets oxidised *in situ* fibre to its parent insoluble form, ensuring high standard colour fastness^{6,7}.

Application of sodium hydrosulphite is being criticized due to the formation of noneco-friendly decomposition products, such as sulphide, sulphite, sulphate, thiosulphate and toxic sulphur. Besides, concentrations of sodium hydrosulphite as well as NaOH remain at least four times higher over the stoichiometric requirement⁸. This has led to explore for alternate ecofriendly hydrosulphite-free based reducing agents^{9,10}. These include application of iron (II) salts alongwith gluconic acid and NaOH at 60°C¹¹, iron (II)

salts in combination with tartaric or citric acid, triethanolamine and NaOH at room temperature¹²⁻¹⁴.

With the increasing demand on textile manufacturers to reduce pollution in textile coloration and finishing, the use of enzymes in the textile chemical processing is rapidly gaining wide recognition because of their ecofriendly and non-toxic characteristics¹⁵. Certain specific enzymes are found to be useful in assisting catalytic reduction of dyes^{16,17}. The effectiveness of enzymes, especially those belonging to oxido-reductase and hydrolase classes, is of utmost importance in this perspective¹⁸. Catalase (EC 1.11.1.6) belonging to oxido-reductase class is being used in textile bleaching¹⁹, sterilization of liquid food products, electronics and conversion of residual hydrogen peroxide to oxygen and water²⁰.

Catalase holds an important place in the enzymatic world because of its potential use in various industries. Catalase has highest turnover among all enzymes known till date; each molecule of catalase can convert 40000 molecule of H_2O_2 into water and molecular oxygen²¹. Catalase (EC 1.11.1.6) is a tetramer of four polypeptide chains, each comprising over 500 amino acids. It contains four porphyrin heme groups that allow the enzyme to react with hydrogen peroxide²². Catalases contain heme group in their structure so they are called as heme catalases and are of 3 types. Catalase-peroxidase contains both peroxidase and catalase activity. Manganese (Mn)-catalase contains Mn in place of Fe (iron) in its catalytic centre so they are called

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pseudo-catalase²¹. Natural fabrics such as cotton are normally bleached with hydrogen peroxide; catalase is used to break down hydrogen peroxide bleaching liquor into water molecules and less reactive gaseous oxygen²³. Catalase may be used in solution and in tablets forms. In food industry, catalase is applied to remove residual H₂O₂ after the processes of cold sterilization of beer, drinks, dairy produce²⁴ beside numerous other applications in food science, industrial food production and medical and analytical fields²⁵.

In the present work, the effectiveness of alkaline catalase along with iron (II) salt has been studied on the reduction and solubilization of vat dyes, thus attempting to substitute sodium hydrosulphite in the vat dyeing technology to make the process ecofriendly. The reduction potential and dye strength, as well as stability of hydrosulphite and alkaline catalase-based dyebaths have also been studied; colour fastness of dyeing is evaluated and compared.

2 Materials and Methods

2.1 Materials

Thoroughly pretreated and bleached cotton fabric (EPI 124, PPI 92, warp and weft count 37^s and GSM 138) was used in this study.

2.2 Chemicals

Alkaline catalase (Ultrox EPN conc liquid) was procured from Rossari Biotech, India. Sodium hydrosulphite (AR, 87-88%), sodium hydroxide (AR, 98%), ferrous sulphate (AR, 98%) and hydrogen peroxide (30%) (SDFCL, Mumbai) were used. Ten different vat dyes of commercial grade, viz. Olive Green B (Vat Green 3, CI 69500), Gold Orange 3G (Vat Orange 15, CI 69025), Yellow 5G (Vat Yellow 2, CI 67300), Green XBN (Vat Green 1, CI 59825), Red 6B (Vat Red 10, CI 67000), Brown BR (Vat Brown 1, CI 70800), Brown R (Vat Brown 3, CI 69015), Olive R (Vat Black 27, CI 69005), Grey M (Vat Black 8, CI 71000) and Blue BC (Vat Blue 6, CI 69825) were used in this study. These dyes were supplied by Atic and I.D.I, India.

2.3 Equipment

Dye strength (*K/S*) and CIELab values were assessed using Computer Color Match (Data color Check, Data color International, US); colour fastness of dyed cotton was assessed according to AATCC test methods 16-2004 (light), 61-2007 (wash), 8-2007 (rubbing) using ATIRA light fastness tester (Paresh

Engineering Works, Ahmedabad, India), wash fastness tester (RBC Electronics, Mumbai) and crock meter (Paramount, Delhi) respectively. Dyebath pH and redox potential were assessed using digital pH meter and digital combined oxidation reduction potential (ORP) meter (Century Instruments, Chandigarh) respectively. The redox potential was assessed at reduction/dyeing temperature using the reference electrode (Ag/AgCl) and the combined electrode (Pt-Ag/AgCl) filled up with saturated KCl solution.

2.4 Dyeing of Cotton

2.4.1 With Sodium Hydrosulphite

Dye bath was prepared with vat dye (1%, owf) pasted with Turkey Red Oil and hot water was added to it. Sodium hydroxide (10%, owd) and sodium hydrosulphite (10%, owd) were added and stirred well until reduction and solubilization of dye took place in the next 15-20 min at 60°C. Cotton fabric was dyed in this bath for 60 min at 60°C. The bath was dropped; dyed cotton was cold washed and oxidized with hydrogen peroxide (1-2 g/l each) at 50-60°C for 20-30 min followed by soaping at boil for 15-30 min and final wash. Dyeing and after-treatments were carried out with a liquor ratio of 1:25 for all treatments separately, except washing.

2.4.2 With Alkaline Catalase along with FeSO₄

Vat dyebaths were prepared with vat dye (1-1.5%, owf), alkaline catalase (0.25-1.5%, owd), ferrous sulphate (1-5%, owd) and sodium hydroxide (10-20%, owd) at 90°C for one hour, keeping MLR 1:25. Cotton was dyed in these baths; dyed samples were thoroughly cold washed, oxidized with hydrogen peroxide followed by soaping and washing.

2.5 Stability of Reduction Bbaths

To study the stability of baths in the absence of dye, reduction baths were prepared separately with hydrosulphite and alkaline catalase along with iron (II) salt. The change in pH and reduction potential were noted down after storing for a specific time at 60°C for hydrosulphite system and at 90°C for alkaline catalase along with iron (II) salt system. Thereafter, dye (Green XBN, 1%) was added in each bath. Cotton fabric was dyed in these baths as mentioned earlier and dye strength was assessed. In practice, fresh dyebaths meant for dyeing are not used immediately in some cases, and time lapse

occurs due to various reasons; even exhausted dyebaths are sometimes not drained out, rather fortified for spent chemicals and dye for reuse of the bath. To study the potential of stored dye baths towards successful dyeing, reduction baths were prepared in hydrosulphite and alkaline catalase systems followed by the addition of dye and storing for 24 h.

2.6 Evaluation of Dyebath and Dyed Cotton

Cotton dyed with both hydrosulphite and alkaline catalase along with iron (II) salt based dyebaths were evaluated for dye strength and colour fastness, while reduction baths were evaluated for the reduction potential as well as *pH* at various stages of dyeing, i.e. in blank reduction bath, after reduction of dye and at the end of dyeing.

3 Results and Discussion

3.1 Dyeing of Cotton with Vat Dye using Sodium Hydrosulphite

Cotton was dyed with ten different vat dyes (1%, owf) using $\text{Na}_2\text{S}_2\text{O}_4$ (10%, owd) and NaOH (10%, owd) followed by oxidation with H_2O_2 . The reduction potential and *pH* at different stages of dyeing as well as dye strength on cotton are reported in Table 1.

The dye bath *pH* at different stages of dyeing is found to be similar, showing adequate alkalinity of the bath required for dyeing (Table 1). The reduction potential of the baths remains on the higher side with slight fall after dyeing, but it is adequate for reduction of vat dyes as well as retaining reduce state of dye throughout dyeing. The dye strength of the samples is found to be as per expectations. These dye strength values are accepted as control values for studying with enzymes in subsequence stages.

3.2 Reduction with Alkaline Catalase

In order to develop new enzyme based reduction method, vat dye baths prepared with vat green XBN (1%, owf), alkaline enzymes (0.25%, owd) and NaOH (10%, owd) neither could develop required reduction potential in bath, nor any dye uptake on cotton at 60°C. Vat dyes require a reduction potential around -750 to -1000 mV for their reduction and dyeing. It is known that the activity of certain enzymes can be synergized by adding metal salts in alkaline dyebaths, which performs two functions, viz. forms $\text{Fe}(\text{OH})_2$ which, in turn, gets partially solubilized in the bath in presence of excess alkali; synergize reduction of vat dye possibly by contributing to the gross reduction potential of bath. Keeping this in mind, FeSO_4 is added in alkaline catalase based reduction baths to enhance reduction potential of dyebaths. It is observed that on addition of FeSO_4 (1%) in the bath, dyeing takes place, though not up to satisfactory level (*K/S* 0.5).

In subsequent study, dyebath temperature was varied to 30, 40, 50, 60, 70, 80 and 90°C, keeping other chemical formulations unchanged. Increase in temperature progressively increases dyebath reduction potential and the maximum dye uptake takes place only at 90°C (*K/S* 0.7). This temperature (90°C) has been accepted for further study. Catalase is a cultured bacterial enzyme, frequently used in bleaching of cotton to remove excess H_2O_2 at boil, and obviously the increase in temperature has enhanced its activity to improve reduction potential of bath.

Obviously, concentrations of catalase, dye, FeSO_4 , NaOH, etc as well as temperature of dyeing are optimized in the next step to achieve optimum dye strength. The optimized concentrations of alkaline catalase, FeSO_4 and NaOH are found to be 1.25%, 4%

Table 1 — Dye bath status and dye strength in sodium hydrosulphite system

Vat dyes	<i>pH</i>			Reduction potential, mV			Dye strength <i>K/S</i>
	Before dye reduction	After dye reduction	At the end of dyeing	Before dye reduction	After dye reduction	At the end of dyeing	
Olive Green	12.9	12.9	12.8	-858	-847	-768	10.6
Gold Orange	12.9	12.9	12.7	-835	-824	-754	6.7
Yellow 5G	12.9	12.9	12.7	-858	-848	-769	10.3
Green XBN	12.9	12.9	12.8	-864	-857	-772	21.0
Red 6B	12.9	12.9	12.8	-860	-854	-780	7.9
Brown BR	12.9	12.9	12.8	-858	-850	-770	7.1
Brown R	12.9	12.8	12.8	-855	-843	-749	8.0
Olive R	12.9	12.9	12.8	-841	-825	-745	4.1
Grey M	12.8	12.8	12.7	-811	-803	-740	2.2
Blue BC	12.8	12.8	12.7	-815	-810	-736	10.8

and 20% respectively at 90°C for 1 h. Subsequently, cotton is dyed with ten vat dyes using these optimized parameters. The dyebath status and corresponding dye strength of cotton are shown in Table 2.

In general, reduction potential as well as pH of all the dyebaths during dyeing cotton with all ten dyes are found adequate to reduce vat dyes completely (Table 2), though cotton dyed with Olive Green, Gold Orange 3G, Green XBN, Red 6B and Olive R shows dye strength equivalent and more than those in hydrosulphite system. Remaining dyes show the dye strength less than that in hydrosulphite system (Fig. 1).

Dye strength on cotton for rest five dyes is found around 33% lesser, but that is not because of the low reduction potential of dyebath, as evident from respective data in Table 2. Because, in case of low reduction potential, no dye reduction could have been observed. It is difficult to say why dye strength is getting reduced for these five dyes in spite of adequate reduction potential marked by standard dye strength for other dyes. This is completely new, ecofriendly and sustainable technology which requires further study. Hence, for these dyes, the concentration of dye in bath is increased from 1% to 1.5% and the K/S for these dyes is shown in Fig. 2. The dye strength of these dyes is found equivalent and more than that of cotton dyed with vat dyes in hydrosulphite system except Blue BC.

3.3 Stability of Reduction Baths

3.3.1 In Absence of Dye

The stability of reduction baths prepared with hydrosulphite and alkaline catalase along with iron (II) salt separately has been studied in absence of dye. For this purpose, reduction baths are prepared in both the systems and then stored for specific time at 60°C and 90°C respectively. The change in pH and reduction

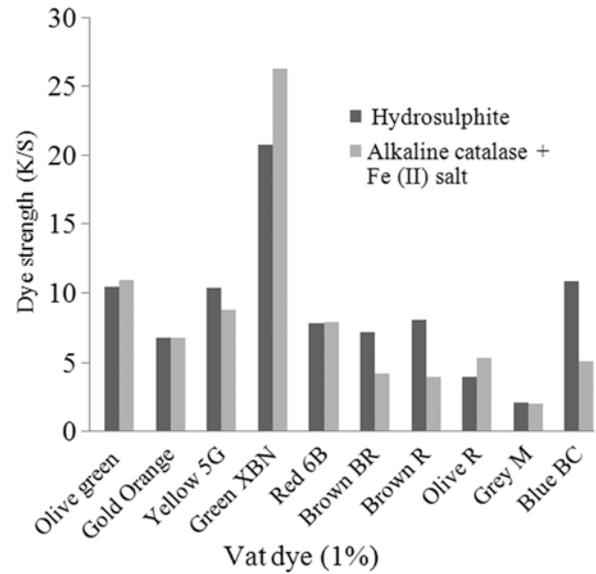


Fig. 1 — Comparison of dye strength on cotton in hydrosulphite and alkaline catalase based reduction baths for 1% shade

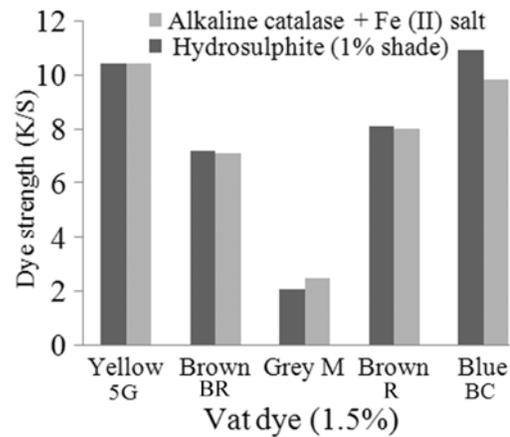


Fig. 2 — Comparison of dye strength on cotton in hydrosulphite system for 1% shade and in alkaline catalase based reduction baths for 1.5% shade

Table 2 — Influence of alkaline catalase on dyebath status and dye strength with vat dyes at 1.0%

Vat dyes	pH			Reduction potential, mV			Dye strength K/S
	Before dye reduction	After dye reduction	At the end of dyeing	Before dye reduction	After dye reduction	At the end of dyeing	
Olive Green	13.6	13.6	13.5	-832	-806	-794	11.0
Gold Orange	13.6	13.6	13.5	-822	-791	-771	6.8
Yellow 5G	13.6	13.6	13.5	-824	-786	-766	8.9
Green XBN	13.6	13.6	13.5	-830	-805	-792	26.3
Red 6B	13.5	13.5	13.5	-822	-798	-764	8.0
Brown BR	13.5	13.5	13.4	-805	-792	-761	4.2
Brown R	13.6	13.6	13.5	-818	-777	-759	4.0
Olive R	13.5	13.5	13.5	-828	-779	-765	5.4
Grey M	13.6	13.6	13.5	-787	-757	-743	2.0
Blue BC	13.5	13.5	13.5	-777	-752	-737	5.5

potential are noted down after storing for specific time, thereafter dye (Green XBN, 1%) is added in each bath. Cotton fabric is dyed in these baths for one hour and dye strength is assessed.

Hydrosulphite based reduction baths retain their reducing capability till 4 h only, beyond which the bath stability goes on reducing. This is due to oxidative and thermal decomposition of hydrosulphite causing loss of it over the time with partial reduction of dye, resulting in obvious less dye strength. In contrast, alkaline catalase based reduction baths retain their reducing capability till 24 h of storage, in general, in the absence of dye in terms of reduction potential and pH both because of non-oxidizing nature of catalase (Table 3).

For hydrosulphite based baths, reduction potential is maximum at the time of preparation of bath i.e. 0 h of storage, but thereafter shows gradual fall in it. The potential values of baths remain quite effective for reduction of dye upto a storage time of zero hour though the reduced status could not be maintained till the end of dyeing. Only the bath stored for one hour shows effectiveness to completely reduce dye and retains the reduced status till the end of dyeing, as marked by dye strength values [Fig. 3(a)]. However, alkaline catalase based baths show stability upto 4 h and then shows gradual slight fall over 24 h, though pH remains as high as 13.2-13.6 for all the stored baths. The dye strength is also found to be maximum for a storage time of 4 h [Fig. 3(a)].

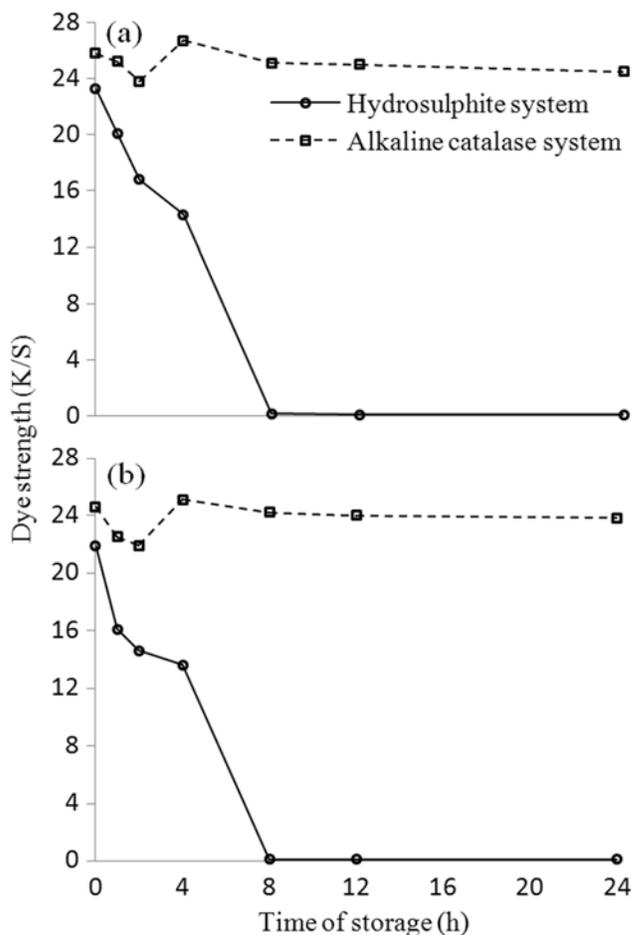


Fig. 3 — Stability of dye baths in (a) absence and (b) presence of dye

Table 3 — Stability of hydrosulphite based and alkaline catalase based reduction bath in absence of dye

Time, h	pH			Reduction potential, mV		
	Before dye reduction	After dye reduction	At the end of dyeing	Before dye reduction	After dye reduction	At the end of dyeing
Hydrosulphite						
0	13.1	13.1	12.7	-869	-858	-768
1	12.9	12.9	12.9	-859	-852	-168
2	12.9	12.9	12.8	-848	-841	-155
4	12.9	12.9	12.8	-842	-831	-143
8	13.0	13.0	12.8	-581	-487	-128
12	12.9	12.9	12.7	-091	-089	-088
24	13.0	13.0	12.7	-064	-063	-080
Alkaline Catalase + Fe(II) Salt						
0	13.6	13.6	13.6	-840	-819	-795
1	13.5	13.5	13.5	-818	-800	-781
2	13.5	13.5	13.4	-808	-788	-775
4	13.5	13.5	13.4	-844	-820	-798
8	13.5	13.5	13.4	-821	-797	-780
12	13.5	13.5	13.3	-798	-767	-746
24	13.5	13.5	13.2	-776	-749	-739

3.3.2 In Presence of Dye

In practice, fresh dyebaths meant for dyeing are not used immediately in some cases and some time lapse occurs due to various reasons; even exhausted dyebaths are sometimes not drained out rather fortified for spent chemicals and dye for reuse of bath. To study potential of stored dyebaths towards successful dyeing in presence of dye, reduction baths are prepared in hydrosulphite and alkaline catalase along with iron (II) salt systems followed by addition of dye (Green XBN, 1%, owf) and storage upto 24 h. The dyebaths in hydrosulphite system show required reduction potential throughout dyeing up to a storage time of 4 h, beyond which though the starting reduction potential remains adequate enough, the end potential (potential after dyeing) starts falling progressively (Table 4), indicating gradual fall in stability of reduced dye towards the end of dyeing.

The dye strength of cotton from all the stored baths could be seen in Fig. 3(b). A maximum dye strength of cotton from hydrosulphite based dyebaths is found at zero hour followed by gradual fall upto 4 h. After that progressive fall in dye strength is observed while dye strength of cotton is maximum after storage for 4 h in alkaline catalase based baths. Thereafter, it shows slight decrease upto 24 h with comparable dye strength values (Table 4). As mentioned earlier, enzymes are catalysts possessing no reducing and oxidising property by themselves, retaining full capacity over time of dyeing.

Table 4 — Stability of hydrosulphite based and alkaline catalase based dyebath in presence of dye

Time, h	pH		Reduction potential, mV	
	Before dyeing	At the end dyeing	Before dyeing	At the end dyeing
Hydrosulphite				
0	13.2	12.9	-861	-758
1	13.0	13.0	-848	-197
2	13.2	13.2	-834	-170
4	13.3	13.2	-778	-150
8	13.2	13.1	-491	-128
12	13.3	13.1	-109	-105
24	13.2	13.0	-103	-100
Alkaline Catalase + Iron (II) Salt				
0	13.6	13.6	-835	-802
1	13.6	13.5	-822	-792
2	13.5	13.5	-820	-787
4	13.5	13.4	-842	-804
8	13.5	13.4	-824	-786
12	13.4	13.3	-778	-741
24	13.2	13.1	-770	-727

3.4 Fastness Performance

The findings show that there is almost no influence on the color fastness to light, wash and rubbing (dry and wet) of dyed cotton for the sodium hydrosulphite and alkaline catalase systems. The light fastness of dyed cotton remains very good to excellent and almost same in both the systems for all ten dyes under study, except for Brown R and Blue BC (Fig. 4).

Both hydrosulphite and alkaline catalase systems show very good wash fastness (Fig. 5). In dry rubbing test, cotton dyed with 10 dyes shows almost same

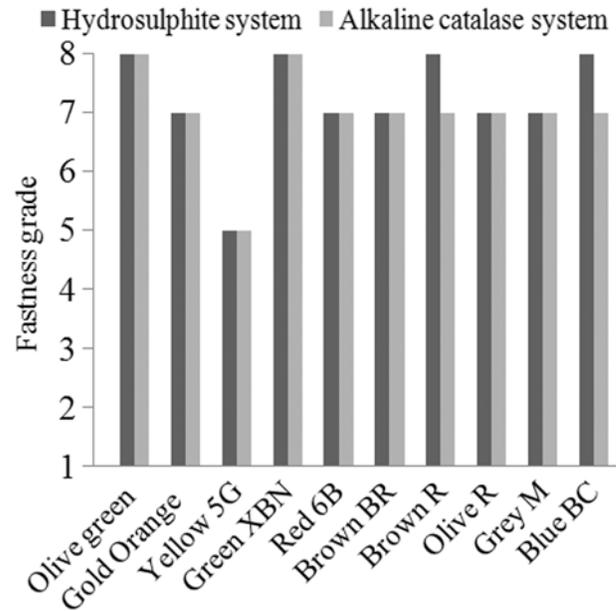


Fig. 4 — Comparison of light fastness

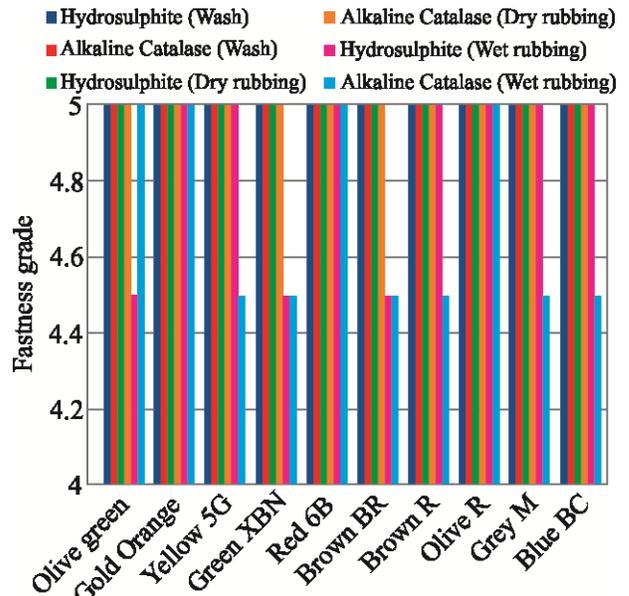


Fig. 5 — Comparison of wash and dry/wet rub fastness

fastness in both hydrosulphite and alkaline catalase systems (Fig. 5). In wet rubbing, cotton dyed with 10 dyes shows identical fastness in both hydrosulphite and catalase systems. Overall, colour fastness of cotton dyed in alkaline catalase system shows good comparative performance with those dyed in hydrosulphite system.

4 Conclusion

Cotton dyed with vat dyes shows comparable dye bath potential in both the hydrosulphite and alkaline catalase along with iron (II) salt based reduction systems. However, out of ten vat dyes studied, dye strength values with Olive Green, Gold Orange 3G, Green XBN, Red 6B and Olive R show comparable or better results with those obtained in hydrosulphite system. Dye strength with Yellow 5G, brown R, Brown BR, Grey M and Blue BC remain on lower side and the shade is found to be increased to 1.5% to achieve results comparable to hydrosulphite system for these five dyes. Hydrosulphite and hydroxide combination generated reduction potential in the range of -811 to -864 mV, which could effectively reduce all vat dyes to the required extent. In contrast, the alkaline catalase along with iron (II) salt could generate a reduction potential around -777 to -832 mV, which is little less to those in hydrosulphite system. Probably because of this, dye molecules of few dyes could not be reduced upto maximum extent causing lesser dye uptake. The stability of reduction baths in the presence and absence of dye shows the same pattern, i.e. fair stability for zero hour in the hydrosulphite system and 24 h in the alkaline catalase along with iron (II) salt system. The color fastness of dyed cotton is found to be excellent and quite comparable for both the reducing systems. It is possible to formulate alkaline catalase along with iron (II) salt based reduction baths to achieve almost the same dye bath features, namely high dye strength of cotton with excellent colour fastness. This is a completely innovative ecofriendly technology for vat dyeing, but it requires further investigation to confirm the case.

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