# A Novel Approach for the Reuse of the Textile Bleaching Wastewater

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***Abstract***-In this paper, the efficiency of used hydrogen peroxide ($H_2O_2$) bleach bath was assessed for the elimination of hydrolyzed unfixed reactive dyes from cellulosic fabrics. The aim of this study was to reuse textile wastewater and develop a new textile dyeing and wash-off method with small quantities of water and chemicals, without compromising quality of dyeing. For this purpose, spent bleach bath having $H_2O_2$ was collected from a textile industry and used in wash-off step of fabric after dyeing with reactive dyes to determine colour fastness properties and shade strength of selected reactive dyes. Five dyeings were carried out, using C. I. Reactive Yellow 138, C. I. Reactive Orange 122, C. I. Reactive Red 195, C. I. Reactive Blue 221, and C. I. Reactive Black 5 and dyed samples were passed through both conventional wash-off and new wash-off method containing spent bleach bath. Washing fastness, rubbing fastness, change of colour, and magnitude of total colour difference ($\Delta E^*$) values of both washed-off fabrics were compared. The colourfastness properties and final shade of fabrics washed-off with spent bleach were found to be comparable to those washed-off conventionally. This study concludes that spent bleach bath containing $H_2O_2$ is a potential nominee for the removal of hydrolyzed reactive dyes from cotton fabrics.

***Keywords***-Bleaching, Textile Dyeing, Wash-off, $H_2O_2$, Wastewater, Colour Fastness

## I. INTRODUCTION

Textile industry is one of the most polluting sectors of Pakistan accounting the amount of fresh water used during the operations of industry and amount of wastewater discharged after the operation [i-ii]. Major environmental problems of textile sector are related to this water consumption and discharge [iii-iv]. Cellulosic fibres are most commonly dye with reactive dyes because of their high colour fastness and ease to apply [v-vii]. These dyes have strong affinity with cotton because their reactive groups make covalent bond with cotton [viii]. Still these dyes have high affinity with water, so fixation reaction is stalled by dye hydrolysis leaving unfixed dyes [v], [vii], [ix-x]. The reactions of reactive dye are shown in Fig. 1.

These hydrolyzed dyes are necessary to remove from dyed material to obtain acceptable colour fastness properties and shade strength. Wash-off process is carried out for the removal of all the excess/unfixed dyes and other chemicals used in the dyeing process. Conventional wash-off method is carried out in many steps at high liquor ratio including hot and cold wash, soaping agents and acid. Thus this step is highly water demanding process of textile industry [xi-xii]. In the past, textile wastewater has been reused in dyeing and finishing after biological treatment, and treatments based on ultrafiltration and membrane technologies [xiii-xiv]. Furthermore, several researchers have tried to reduce water consumption in washing process by developing special washing detergents, cationic fixing compounds, and easy-to-wash dyestuffs [xi], [xv-xvi].

In this novel research effectiveness of used bleach bath having hydrogen peroxide ($H_2O_2$)in wash-off as washing agent to remove unfixed dyes from material was accessed. In industry bleaching of cotton is widely achieved by using $H_2O_2$ as bleaching agent [xvii]. $H_2O_2$ dissociate at high pH (10-12), forming per hydroxyl anions ($HO^-_2$) refer to (1) which is responsible for bleaching action [xviii].

$$H_2O_2 \rightleftharpoons H^+ + HO^-_2 \quad (1)$$

The results achieved in the present study propose that conventional wash-off method can be replaced by spent bleach bath as washing agent without compromising colour fastness and colour strength. By this novel method water and energy consumption and pollution load will be reduced.

## II. MATERIALS & METHOD

### 2.1 Materials

In this study, 100% cellulosicknitted fabric of single jersey construction and 200 g/m$^2$weight was used. Five reactive dyes used in the study are given in Table I. Chemicals used for dyeing like sodium chloride (NaCl) and sodium carbonate ($Na_2CO_3$),were of commercial grade and used without any further purification.

*2.2 Methods*

*2.2.1 Dyeing and washing*

All dyeing was carried out with 5% o.w.f (on weight of the fibre) of dyes to obtain dark shades. In all trials fabric of 20g divided into four swatches, each of 5g weight was used.The dyeing was carried out in an IR (infra red) laboratory dyeing machine (Datacolour, Ahiba Nuance) at a liquor ratio of 1:8, in the presence of 80 g/L NaCl and 20 g/L $Na_2CO_3$.

All samples were dyed at 60ºC for 60 minutes according to isothermal all-in-one laboratory method. After dyeing samples were taken out from dyeing machine, rinsed in tap water and exposed to wash-off treatment. One swatch of fabric from each dyeing sample was washed-off with conventional methods shown in Table II. This swatch was treated as reference sample.

TABLE II
CONVENTIONAL WASH-OFF METHOD

| Step | Washing Steps | Temp. (ºC) | Time (min) |
|---|---|---|---|
| 1 | Cold rinse | 30 | 10 |
| 2 | Neutralization with $CH_3COOH$ | 30 | 10 |
| 3 | Warm Wash | 50 | 10 |
| 4 | Hot Wash | 80 | 10 |
| 5 | Soaping | 85 | 10 |
| 6 | Cold rinse | 30 | 10 |

The remaining three swatches of fabric were subjected to new wash-off method consisted of 1 to 3 washing stepsusing 100% spent $H_2O_2$ bleach bath, as shown in Table III. First, second, and third fabric swatches underwent washing step 3, steps 3-4, and steps 3-5, respectively. After the completion of wash-off process, samples were removed from the machine, squeezed, dried, and conditioned for 24 hours before evaluation ofthe uniformity of dyeing, change of shade and colour fastness properties.

TABLE III
NEW WASH-OFF METHOD USING SPENT $H_2O_2$ BLEACH BATH

| Step | Washing Steps | Temp. (ºC) | Time (min) |
|---|---|---|---|
| 1 | Cold rinse | 30 | 10 |
| 2 | Neutralization with $CH_3COOH$ | 30 | 10 |
| 3 | Wash#1 with spent $H_2O_2$ bleach | 50 | 10 |
| 4 | Wash#2 with spent $H_2O_2$ bleach | 80 | 10 |
| 5 | Wash#3 with spent $H_2O_2$ bleach | 85 | 10 |
| 6 | Cold rinse | 30 | 10 |

*2.2.2 Colour measurement and fastness properties*

The colour fastness of sample fabrics was evaluated using AATCC test methods. AATCC test methods 61-2001-2A and 8-2001 were used to assess colour staining and rubbing fastness respectively [xix], [xx]. Colour difference values between samples washed-off with conventional and new methods were determined using a spectrophotometer (Data colour, Spectra flash SF-600 Plus CT) at the following settings: CIELAB colour equation, Illuminant D65, specular reflection included mode, 10º Standard observer, and aperture size of LAV 30 mm [vi]. After folding each sample twice, four measurements were carried out at different positions on the fabric surface and averaged.

## III. RESULTS AND DISCUSSION

To determine the fastness properties of samples after treating them with the used bleach, they were subjected to different number (1 to 3) of treatments. Table IV shows a comparison of fastness properties of reference and samples washed-off using used $H_2O_2$ bleach water. Similar washing and rubbing fastness was observed in the data after used $H_2O_2$ bleach wash-off. This data was collected on the basis of multi-fiber staining. For C. I. Reactive Yellow 138dyeing, the fabric sample washed-off with spent $H_2O_2$ bleach water showed identical fastness properties, mainly in the range of 4.5 to 5.0 as shown in Fig. 2. The change of shade was found to be 4.5, showing a similar shade compared to that of reference. In case of C. I. Reactive Red 195, the good fastness values confirm that new wash-off method under investigation is effective in removal of all hydrolyzed dyes. Similar trend is followed by all other dyes.

$\Delta L^*$ (difference in lightness), $\Delta c^*$ (change in chroma), $\Delta h^*$ (change in hue), and $\Delta E^*$ *(total colour difference)*values (Table V) are used for the account of colour differences between reference fabric and those washed-off using spent $H_2O_2$ bleach water. Negligible colour difference is observed in all cases i.e. $\Delta E^* < 1.1$.The results apposite to C. I. Reactive Yellow 138demonstratethat 1$^{st}$ wash-off using used $H_2O_2$ bleach water was good enough to achieve similar depth of shade. Negligible differences in lightness ($\Delta L^*$= -0.48), Hue ($\Delta H^*$ = -0.35), and total difference ($\Delta E^*$ =0.51) confirm that colour properties of treated fabric were equivalent to those of the reference sample.

The total colour difference (ΔE*) was further reduced to 0.38 when sample underwent 3rd wash-off.

In the case of C. I. Reactive Red 195, the shade of sample treated with used$H_2O_2$bleachwas found to be slightly darker (ΔL* = -1.12), slightly duller (Δc* = -1.12), and within tolerable total colour difference (ΔE* = 0.77). Results were not improved by further washing so it was concluded that in case of red 195 only one wash using used $H_2O_2$ seems to be sufficient to remove hydrolyzed dye. Values of ΔE for of C. I. orange 122 all three wash-offs were in acceptable limit (ΔE<1.1). For C. I. Reactive Blue 221 and C. I. Reactive Black 5, total colour difference (Δ*E**) values of 0.86 and 0.08 were achieved at 1st wash. These results are previously discussed in similar way [xxi].

A direct relation between the total colour difference (Δ*E**) and number of wash-off treatments is shown in Fig. 2.

## IV. CONCLUSION

A new wash-off method was investigated in this study for the effective removal of deposited hydrolyzed dyes with reduced quantity of fresh water from the cotton fabric. The efficiency of the new method using spent $H_2O_2$ bleach water was investigated on cotton fabrics dyed with C. I. Reactive Yellow 138, C. I. Reactive Red 195, C. I. Reactive Blue 221, C. I. Reactive Orange 122 and C. I. Reactive Black 5indark shades. On the basis of results obtained in this study, it is concluded that similar colour fastness properties with minimal colour difference i.e, 4.5 and with reduced water consumption with respect to conventional dyeing and wash-off process, can be achieved by used $H_2O_2$ bleach based wash-off method. This study concludes that used $H_2O_2$ bleach is a potential candidate for removing the unfixed reactive dyes from cotton fabrics.

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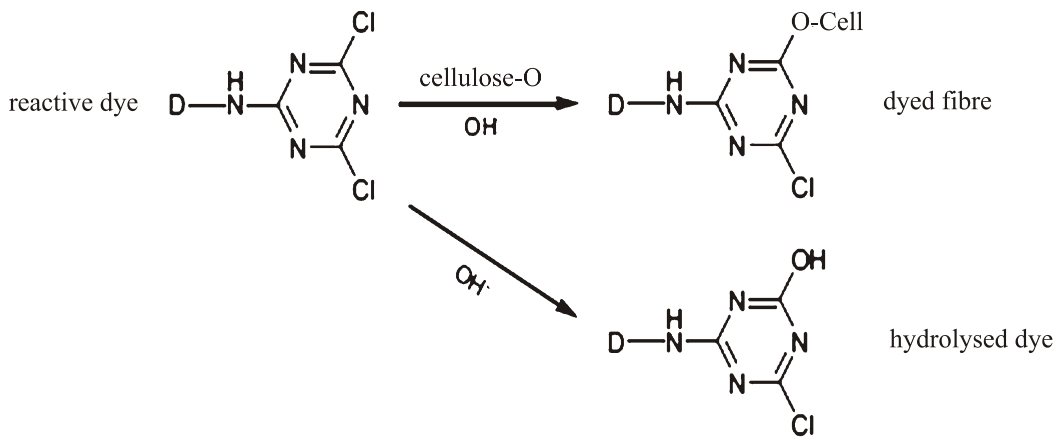



Fig. 1. Reaction of reactive dyes

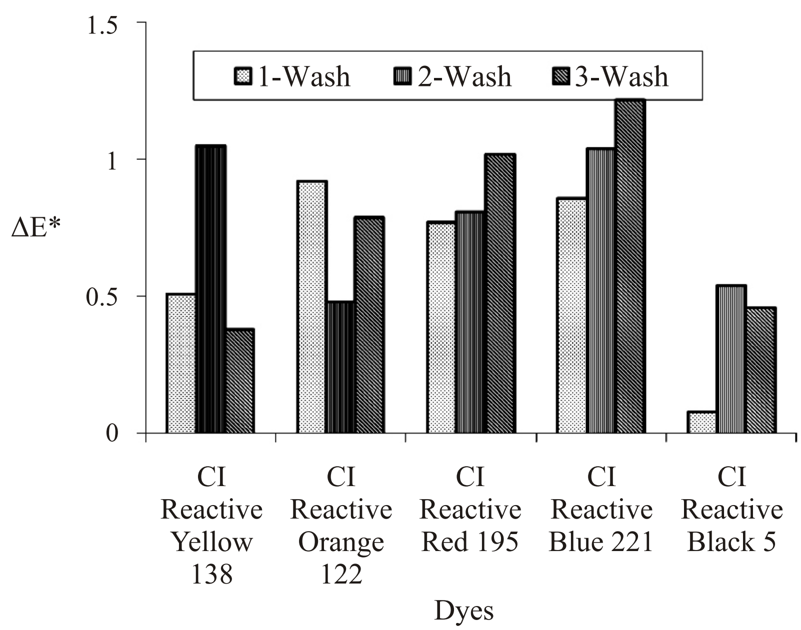



Fig. 2. Effect of washes on total colour change (ΔE*)

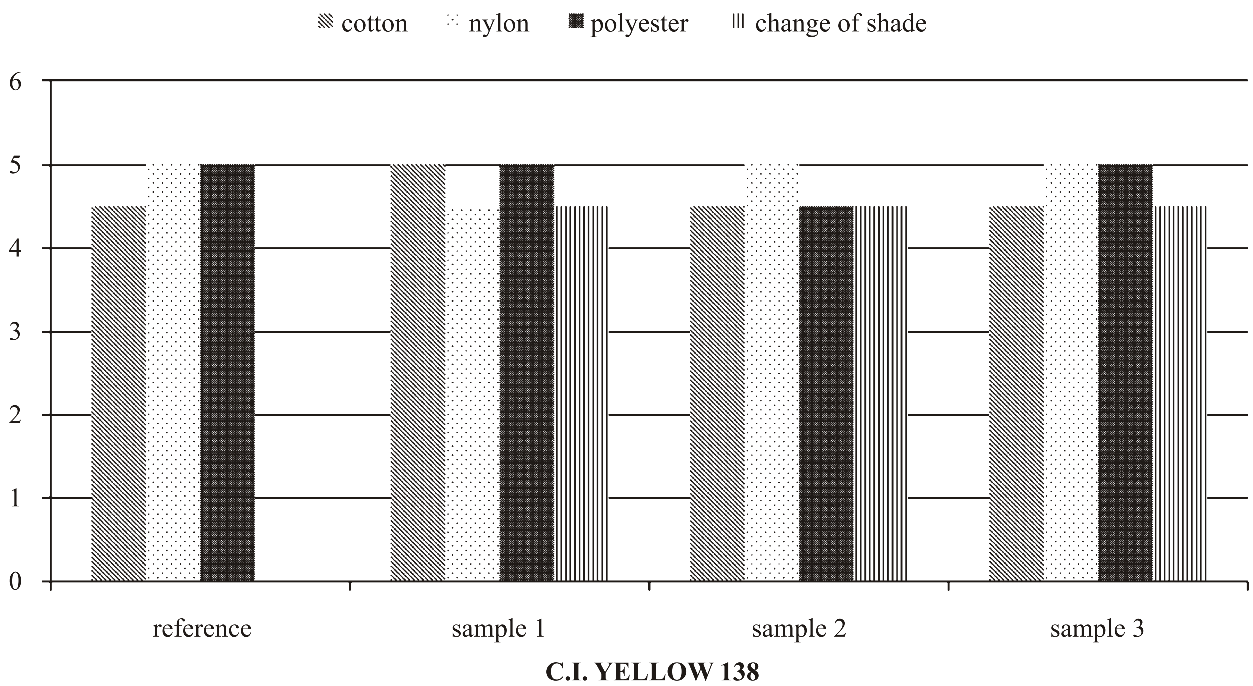



Fig. 3. Effect of reuse washes on wash fastness and change of shade

TABLE I
REACTIVE DYES USED IN THE RESEARCH

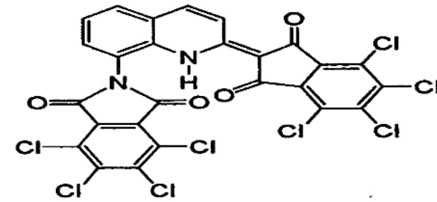
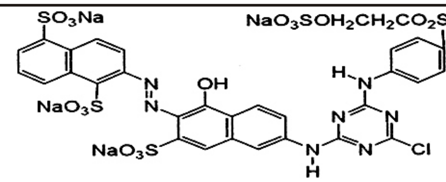
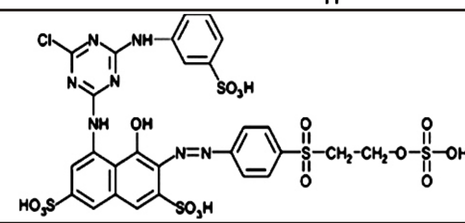
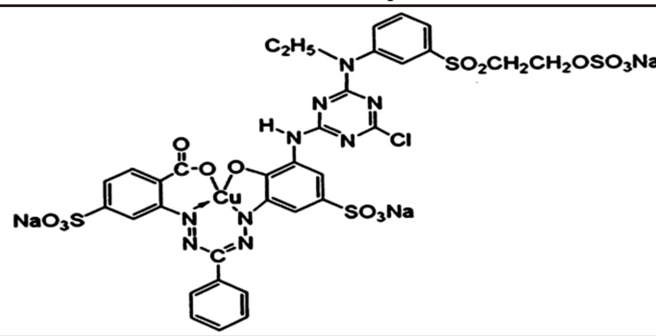
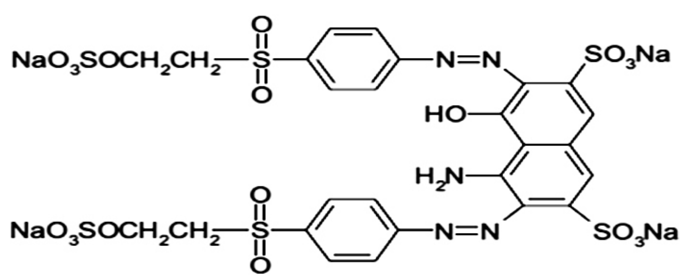
| C. I. name<br>Commercial name<br>Molecular formula<br>Molecular weight (g/mol) | Chemical Structure |
|---|---|
| C.I. Reactive Yellow 138<br>Procion Yellow H-EXL<br>$C_{26}H_{6}Cl_{8}N_{2}O_{4}$<br>693.96 |  |
| C.I. Reactive Orange 122<br>Jakofix Orange ME2RL<br>$C_{31}H_{2}0ClN_{7}O_{16}S_{5}$.4Na<br>1034.25 |  |
| C.I. Reactive Red 195<br>Assofix Red 3BF<br>$C_{31}H_{19}ClN_{7}O_{19}S_{6}$.5Na<br>1136.32 |  |
| C.I. Reactive Blue 221<br>Synozol Blue K-BR<br>$C_{33}H_{24}ClCuN_{9}Na_{3}O_{15}S_{4}$<br>1082.83 |  |
| C.I. Reactive Black 5<br>Sinarcion Black VBS<br>$C_{26}H_{21}N_{5}Na_{4}O_{19}S_{6}$<br>91.82 |  |

TABLE IV
COLOUR FASTNESS PROPERTIES OF SAMPLES WASHED-OFF WITH SPENT $H_2O_2$ BLEACH BATH

| | No of Washes | Crocking | | Multi-fiber staining | | | Change of shade |
|---|---|---|---|---|---|---|---|
| | | Dry | Wet | Cotton | Nylon | Polyester | |
| C.I. Reactive Yellow 138 | | | | | | | |
| Reference | - | 5 | 5 | 4.5 | 5 | 5 | - |
| Sample-1 | 1 | 5 | 5 | 5 | 4.5 | 5 | 4.5 |
| Sample-2 | 2 | 5 | 5 | 4.5 | 5 | 4.5 | 4.5 |
| Sample-3 | 3 | 5 | 5 | 4.5 | 5 | 5 | 4.5 |
| C.I. Reactive Orange 122 | | | | | | | |
| Reference | - | 5 | 5 | 5 | 5 | 4.5 | - |
| Sample-1 | 1 | 5 | 5 | 5 | 5 | 5 | 4.5 |
| Sample-2 | 2 | 5 | 5 | 4.5 | 5 | 5 | 4.5 |
| Sample-3 | 3 | 5 | 5 | 4.5 | 5 | 4.5 | 4.5 |
| C.I. Reactive Red 195 | | | | | | | |
| Reference | - | 5 | 5 | 4.5 | 5 | 5 | - |
| Sample-1 | 1 | 5 | 5 | 4.5 | 4.5 | 5 | 4.5 |
| Sample-2 | 2 | 5 | 5 | 4.5 | 5 | 4.5 | 4.5 |
| Sample-3 | 3 | 5 | 5 | 4.5 | 4.5 | 5 | 4.5 |
| C.I. Reactive Blue 221 | | | | | | | |
| Reference | - | 5 | 5 | 5 | 5 | 5 | - |
| Sample-1 | 1 | 5 | 5 | 5 | 5 | 4.5 | 4.5 |
| Sample-2 | 2 | 5 | 5 | 4.5 | 4.5 | 5 | 4.5 |
| Sample-3 | 3 | 5 | 5 | 4.5 | 5 | 5 | 4.5 |
| C.I. Reactive Black 5 | | | | | | | |
| Reference | - | 5 | 5 | 5 | 5 | 5 | - |
| Sample-1 | 1 | 5 | 5 | 5 | 4.5 | 5 | 4.5 |
| Sample-2 | 2 | 5 | 5 | 5 | 5 | 4.5 | 4.5 |
| Sample-3 | 3 | 5 | 5 | 5 | 5 | 5 | 4.5 |

TABLE V
CIELAB COLOUR DIFFERENCES OF SAMPLES WASHED-OFF WITH SPENT $H_2O_2$ BLEACH BATH AND COMPARED WITH REFERNCE

| Dyes | No of Washes | CIELAB Colour difference values | | | | | |
|---|---|---|---|---|---|---|---|
| | | ΔL* | Δa* | Δb* | Δc* | Δh* | ΔE*cmc |
| C.I. Reactive Yellow 138 | | | | | | | |
| Sample-1 | 1 | -0.48 | 0.88 | 0.87 | 1.19 | -0.35 | 0.51 |
| Sample-2 | 2 | -1.06 | 1.78 | 1.56 | 2.22 | -0.80 | 1.05 |
| Sample-3 | 3 | -0.09 | 0.69 | 0.52 | 0.79 | -0.35 | 0.38 |
| C.I. Reactive Orange 122 | | | | | | | |
| Sample-1 | 1 | 0.00 | -0.62 | 1.06 | 0.39 | 1.16 | 0.92 |
| Sample-2 | 2 | -0.94 | -0.63 | -0.44 | -0.75 | 0.18 | 0.48 |
| Sample-3 | 3 | -1.46 | -0.84 | -0.07 | -0.60 | 0.58 | 0.79 |
| C.I. Reactive Red 195 | | | | | | | |
| Sample-1 | 1 | -1.12 | -1.10 | -0.60 | -1.12 | -0.56 | 0.77 |
| Sample-2 | 2 | -0.67 | -1.02 | -1.21 | -1.06 | -1.17 | 0.81 |
| Sample-3 | 3 | -0.28 | -1.37 | -1.67 | -1.41 | -1.63 | 1.02 |
| C.I. Reactive Blue 221 | | | | | | | |
| Sample-1 | 1 | 0.39 | -0.87 | 0.76 | -0.71 | -0.92 | 0.86 |
| Sample-2 | 2 | 0.04 | -1.08 | 0.97 | -0.89 | -1.14 | 1.04 |
| Sample-3 | 3 | 0.45 | -1.23 | 1.15 | -1.07 | -1.31 | 1.22 |
| C.I. Reactive Black 5 | | | | | | | |
| Sample-1 | 1 | -0.05 | -0.04 | 0.04 | -0.04 | -0.05 | 0.08 |
| Sample-2 | 2 | 0.46 | -0.07 | -0.40 | 0.40 | -0.02 | 0.54 |
| Sample-3 | 3 | 0.44 | -0.11 | -0.06 | 0.07 | -0.10 | 0.46 |

Note: Δ*L** (difference in lightness), Δc* (change in chroma), Δ*h** (change in hue), and ΔE*(difference between two colours in an L*a*b* colour space.)