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Synthesis and Application of Reactive Fluorescent Brightening Agents on UV Irradiated Cotton Fabric

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In present study stilbene based optical brightening agents were synthesized and applied to UV irradiated cotton fiber. Synthesis comprised the condensation between 4,4-diaminostilbene-2,2-disulfonic acid followed by condensation with other substituents such as diethanolmine, metanilic acid, vinyl sulfone paraester and ester prepared by esterification of diethanolamine separately. The synthesized brighteners were applied on UV irradiated and un-irradiated cotton fabric. The UV radiation intensity of 180 watt for 1 h was used. Absorption spectra of these brighteners was recorded using double beam spectrophotometer CECIL CE 7200/Data stream software. CIE whiteness of fabric samples was recorded using spectra flash SF 600/UK. After optical brightening agent's application, the cotton fabric samples were also tested for washing, chlorine and light fastness properties. CIE whiteness was noted to be significantly higher in case of irradiation *versus* unirradiated samples and fastness properties did not changed. On the basis of results, the application of brightening agent on UV irradiated cotton is suggested for the enhancement of cotton fabric properties to enhance the whiteness.

Keywords: Optical brightening agent, CIE whiteness, Stilbene, UV treatment, Cotton fabric properties, Characterization.

INTRODUCTION

Fluorescent whitening agents are merely coloured or colourless compounds that are applied in the form of solution to the substrate. They produce fluorescence by absorbing UV light (200-400 nm) and emitting blue fluorescent light (400-500 nm). Optical brightening agents (OBAs) are also effective in polymer substrates along with textile *e.g.* thermoplastics, styrene polymers, adhesives and other substrates. Textile industry was the first one to involve the use of optical brightening agents. This was mainly for the removal of the yellowish tinge present in the synthetic and natural fiber since they cannot be removed by bleaching agents. Therefore, optical brightening agent is a good option for the brightening such type of material. In textile finishing, solubility and sustainability are the major requirements for application of brighteners. Stilbene derivatives are very effective in this regard due to their higher solubility in water and remarkable light fastness properties[1].

The mode of action of brighteners is fluorescence, *i.e.* absorbing light in UV region (330-380 nm) and re-emit in visible region (400-750 nm). This makes cotton fabric to appear more brighter and brilliant white to human eye. The brightening agents are commonly added to textile substrates at various manufacturing steps in order to increase their apparent whiteness and to provide an additional layer for protection against UV-A and UV-B radiation. UV radiations have low ionization power as compared to X-rays and γ-rays and are very effective in surface modification of textile and natural fabric. The process is of great commercial value, if applied before the application of brighteners[2].

In view of above discussion, it was hypothesized that the application of brightener agent on UV irradiated cotton might enhance the fabric properties and the present study was performed to appraise the effect of brightening agent, applied on UV irradiated cotton fiber. The derivatives of 4,4- diamino-stilbene-2,2-disulfonate namely OBA-1, OBA-2, 0BA-3, OBA-4, OBA-5 were prepared (Fig. 1), applied to UV irradiated cotton fiber followed by fastness studies cotton fiber.

EXPERIMENTAL

Application of optical brightening agents on cotton fabric: Synthesized optical brightening agents were applied on bleached and irradiated cotton fabric. For optimization, brighteners were applied on cotton fabric for different time intervals (10, 20, 30 and 40 min). temperature range of 50-80 °C with difference of 10 °C[3]. CIE whiteness values were noted for each sample using spectra flash (SF-600) at Noor Fatima Fabrics (Pvt.) Ltd. Faisalabad.

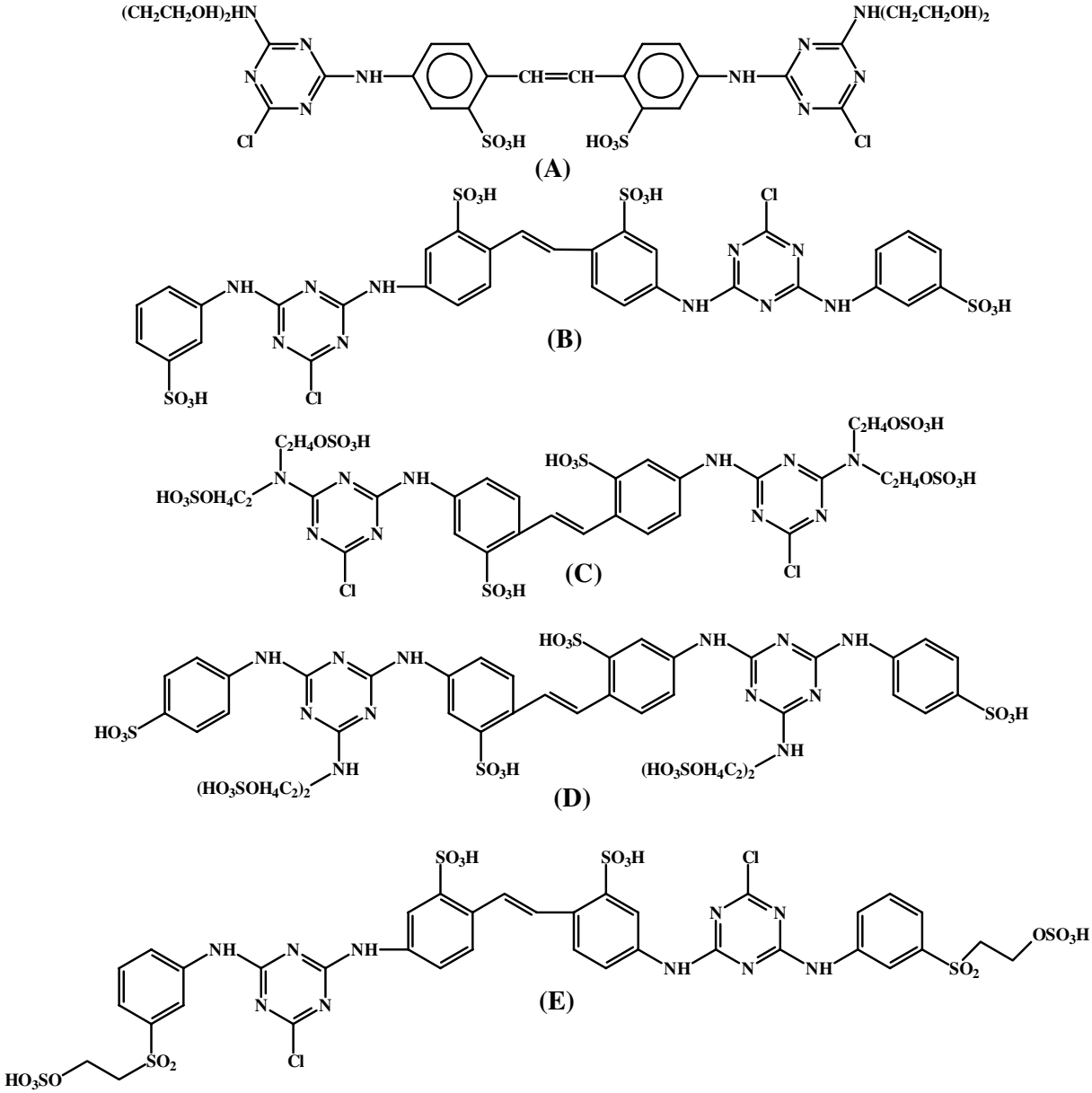

Fig. 1. Structures of synthesized optical brightening agent's: (a) OBA-1, (b) OBA-2, (c) OBA-3, (d) OBA-4, (e) OBA-5

Evaluation of fastness properties: The CIE whiteness Index (WI) values were obtained for optically brightened substrates using the AATCC test method using data colour SF600X spectrophotometer with the following setting: illuminant D65, large area view (30 mm), specular included, UV calibrated and CIE 1964 standard colorimetric observer. The WI were measured at different locations and average whiteness value was recorded.

Determination of absorbance (λ_{max}): Absorbance of the synthesized fluorescent brighteners was determined by using spectrophotometer/DataStream soft ware. A 0.05% solution in distilled water was used for λ_{max} measurement.

RESULTS AND DISCUSSION

CIE whiteness trends of OBA-1 treated, bleached cotton fabric: CIE whiteness (fluorescence quantum yield) values after the application of optical brightening agents on cotton fabric were noted from Spectra Flash/SF-600-UK[4-6]. In case of OBA-1, maximum CIE whiteness was observed when optical brightener was applied on irradiated fabric for 0.5 h (Fig. 2a) (74.5 for IF, 70.5 for UIF). As it is clear from graph that temperature, time and pH affect the CIE values. Whiteness was observed to be greater in case of irradiate fabric and excellent whiteness was achieved when brightener was applied for thirty minutes both in case of irradiated and un irradiated fabric. From the CIE whiteness values trend as shown in Fig. 2b, it was revealed that the fabric sample treated with brightener at 70°C, furnished maximum value of whiteness (78.4 for IF, 75 for UIF). The temperature beyond 70 °C decreased the whiteness values due to breakage of bond formed between fabric and brightener. Regarding pH effect on CIE values, an increase in whiteness was observed as the pH changed from acidic to neutral and then decreased as pH reached to alkaline (Fig. 2c). So, it is clear that stilbene based brighteners may furnished maximum brightness when applied under neutral condition. This increased whiteness in case of application of

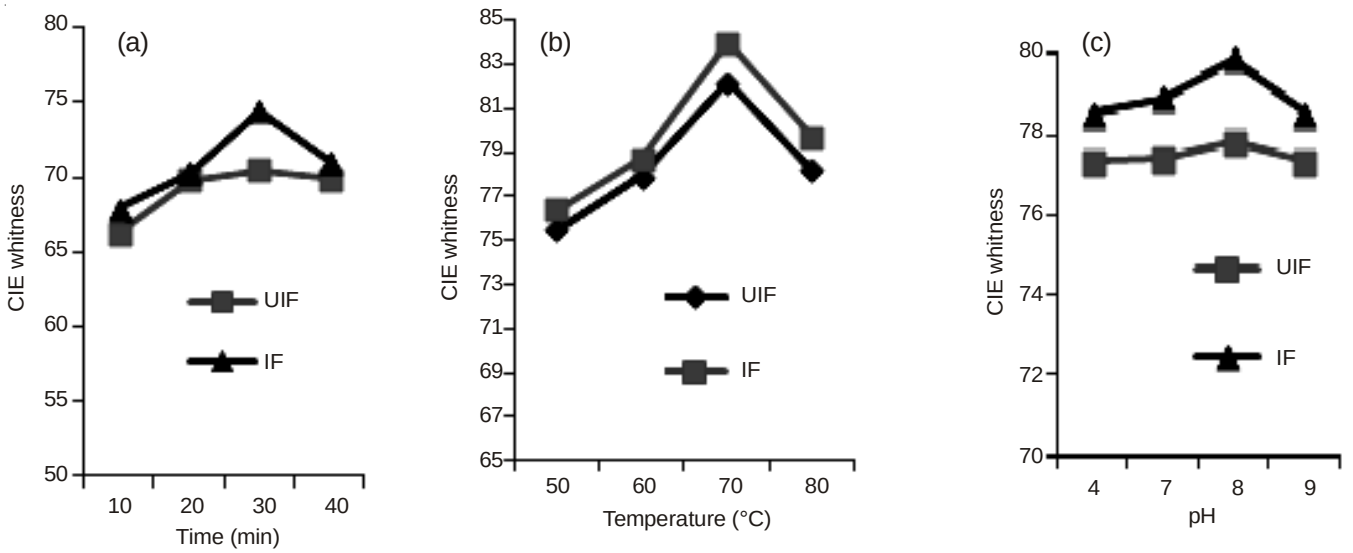

Fig. 2. CIE whiteness of fiber treated with OBA-1 (a) time (b) temperatures (c) various pH, IF = irradiated fiber and UIF = unirradiated fiber

optical brightening agent on irradiated cotton fabric was probably due to the increased surface area by UV radiation treatment given to the fabric. It enhanced the uptake of brightener by the fabric resulting in greater whiteness.

CIE whiteness trends of OBA-2 treated bleached cotton fabric: In case of application of OBA-2 application on bleached cotton fabric, the CIE whiteness value increased. Maximum whiteness was achieved when fabric was dipped in brightener solution for 0.5 h (80.2 for IF, 78.9 for UIF). Here again the whiteness values were higher of irradiated fabric under all the conditions of time application as compared to un-irradiated fabric (Fig. 3a). At low time, the sorption of brightener was incomplete, however, for longer time there might be desorption of OBA-2 and resulted in low whiteness both at short and longer contact. The temperature range studied was 50 to 80 °C and 70 °C was found best temperature for better CIE values (Fig. 3c) and same trend has been reported previously[7]. By increasing the temperature beyond 70 °C, the CIE value decreased. The pH value of 7 showed the best CIE values (Fig. 3b).

CIE whiteness of OBA-3 treated, bleached cotton fabric: In case of OBA-3, the maximum CIE whiteness was observed when irradiated fabric was dipped in irradiated optical brightener solution for 0.5 h (80.8) similar trend was observed in case of unirradiated fabric (79.2). In case of OBA-3, the UV irradiation effect was non-significant (Fig. 4a). The temperature was similar as observed for OBA-1 and OBA-2 (Fig. 4c) and 70°C was found to be better for to enhance the CIE value and the values were at 70° C were 82.1 for IF and 79.9 for UIF. The pH effect was also non-significant (Fig. 4c).

CIE whiteness of OBA-4 treated cotton fabric: The best temperature for OBA-4 was also found to be 70 °C. However, the CIE value was higher versus OBA-1, 2 and 3. By increasing the temperature from 50°C to 70°C, the CIE value increased from 76.5 to 84 (Fig. 5b) and by increasing the temperature to 80 °C, the CIE value decreased. At higher temperature there may be low interaction between fabric and brightener resulting in low CIE whiteness value. In case of OBA-4, the irradiated fabric showed significant effect and maximum value was observed for 0.5 h treatment, whereas un-irradiated fabric showed non-significant effect (Fig. 5a). For OBA-4, the effect of pH on CIE value was also non-significant (Fig. 5c).

CIE whiteness of OBA-5 treated cotton fabric: In case of OBA-5, the maximum values of 83 for irradiated fibre (IF), 81.5 for unirradiated fibre (UIF) were observed for 0.5 h contact (Fig. 6a). Low whiteness at less time interval application

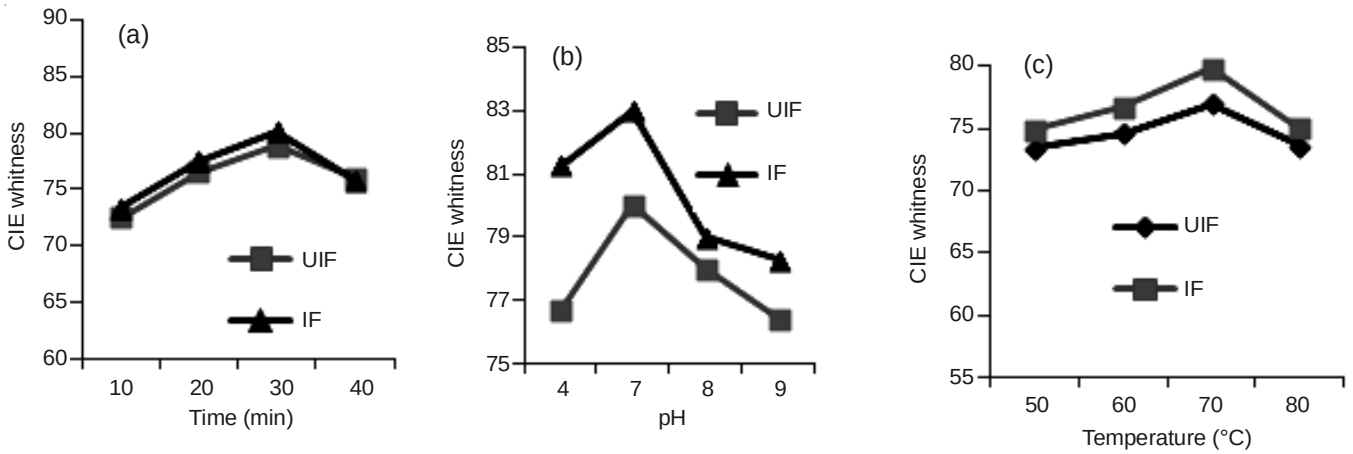

Fig. 3. CIE whiteness of fiber treated with OBA-2: (a) time intervals (b) pH (c) temperature, IF = irradiated fiber and UIF = unirradiated fiber

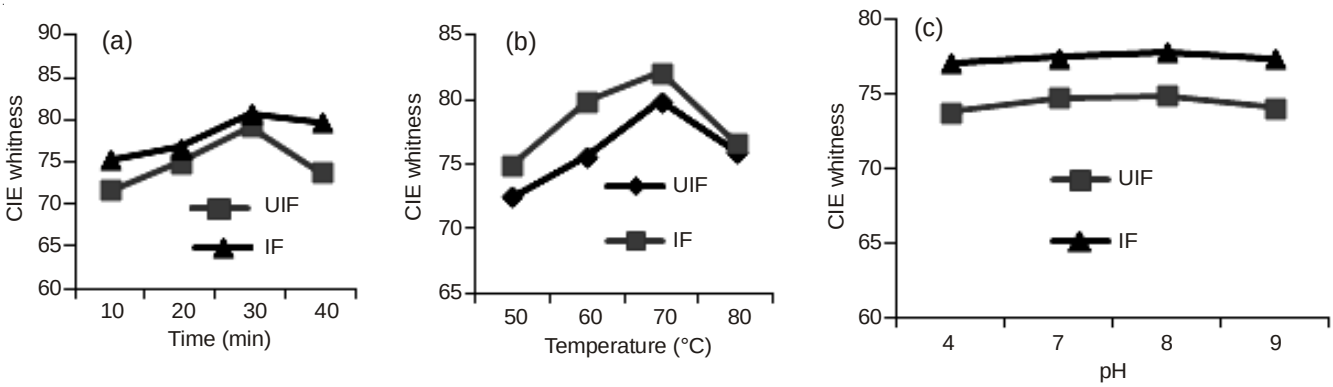

Fig. 4. CIE whiteness of fiber treated with OBA-3 (a) time interval (b) temperature (c) pH

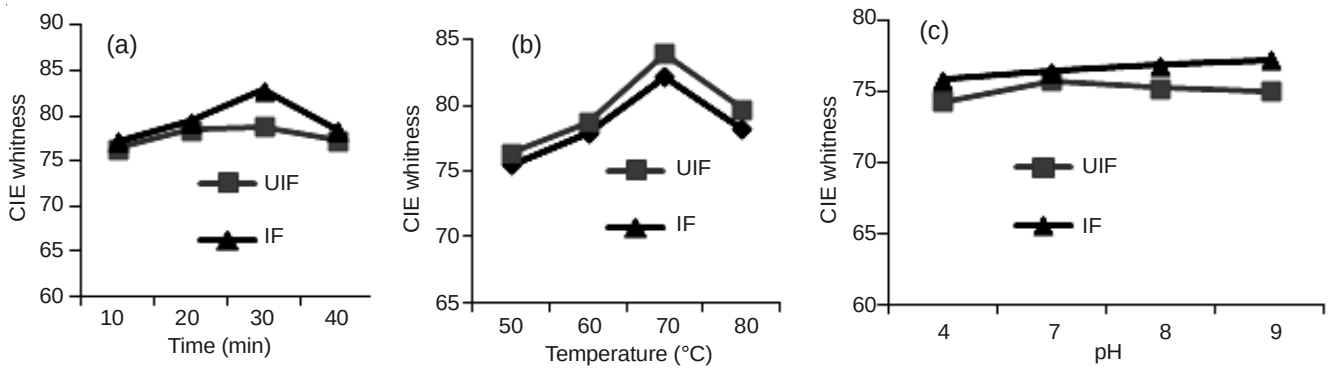

Fig. 5. CIE whiteness of fiber treated with OBA-2 (a) time intervals (b) temperature (c) pH

indicated the less sorption of brightener by the fabric and for longer time contact there might be desorption. It was also reported that longer time contact caused aggregation and formation of second layer of brightener on the fabric resulting in quenching of excited singlet state by the neighboring brightener molecules and resultantly CIE value may decrease[8].

Fig. 6b illustrates the effect of temperature on the application of brightener. The decreased values at elevated temperatures were due to the weakening of bond strength formed between the fabric and fluorescent brightener.

From the above study it was concluded that for the best value of whiteness synthesized stilbene based fluorescent brighteners should be applied at 70 °C and best pH was found to be 8. However, the pH effect was non-significant for the application of OBA-5 (Fig. 6c).

Washing, chlorine and light fastness tests for optical brightening agents: The fastness tests were performed for the sample which showed maximum values of CIE values at optimized conditions of contact time, temperature and pH. The CIE values found to be stable to chlorine, washing and light fastness which indicated that optical brightening agent's applications were effective and all stilbene based brightener showed similar behaviours to chlorine, washing and light fastness (Tables 1-3). The light fastness test revealed brighteners

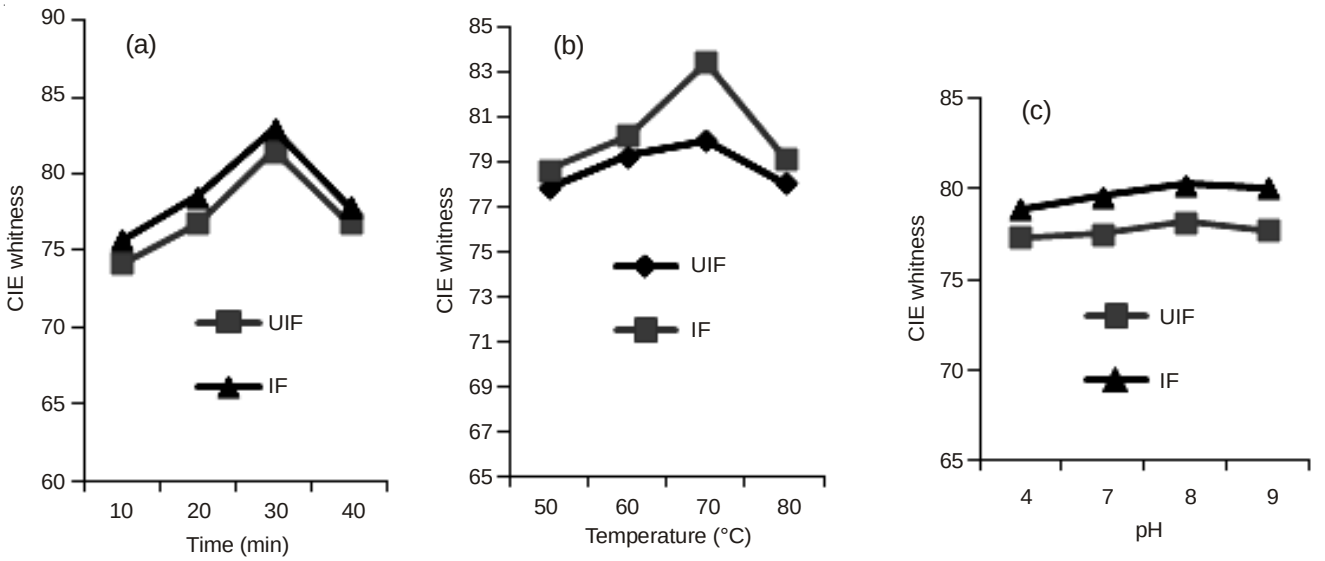

Fig. 6. CIE whiteness of fiber treated with OBA-2 (a) time interval (b) temperature (c) pH

TABLE-1
CIE WHITENESS AFTER WASHING FASTNESS TEST

Parameter	OBA-1	OBA-2	OBA-3	OBA-4	OBA-5
Time (0.5 h)	73.8	78.0	77.6	78.4	74.8
Temp. (70 °C)	76.1	76.9	75.3	79.1	71.0
pH	75.2	75.3	73.0	75.0	76.8

TABLE-2
CIE WHITENESS AFTER CHLORINE FASTNESS TEST

Parameter	OBA-1	OBA-2	OBA-3	OBA-4	OBA-5
Time (0.5 h)	72.0	75.0	76.6	77.4	71.8
Temp. (70 °C)	76.7	75.9	73.3	76.1	77.3
pH	72.2	72.3	71.2	74.8	74.8

TABLE-3
CIE WHITENESS AFTER LIGHT FASTNESS TEST

Parameter	OBA-1	OBA-2	OBA-3	OBA-4	OBA-5
Time (0.5 h)	75.4	76.8	75.6	70.4	74.8
Temp. (70 °C)	74.7	74.9	72.3	73.1	75.3
pH	71.2	71.3	74.2	72.8	71.8

were also stable to light. The absorbance of the synthesized brighteners was noted by using spectrophotometer and shown in the Table-4, which was found to be in the range 350-390 nm which indicated the stability of optical brightening agent's in visible region. Overall, it was observed that the high energy radiation is good option for the modification of cotton fabric to enhance the CIE values with diminishing the cotton fiber properties and processes is also environmental friendly[9,10] and are being in practice in every field of life[11-13].

TABLE-4
ABSORBANCE OF SYNTHESIZED BRIGHTENERS

Brightener	OBA-1	OBA-2	OBA-3	OBA-4	OBA-5
λ_{max}	374	389	362	378	369

Conclusion

Stilbene based optical brightening agents were synthesized through condensation mechanism and applied to UV irradiated cotton fabric. Synthesized optical brighteners were applied on UV irradiated cotton fabric, exhibited better whiteness as compared to un-irradiated cotton fabric. Furthermore, the washing, chlorine and light fastness properties did not changed significantly. The optimized values of contact time, pH and temperature were 30 min, neutral and 70 °C, respectively. From results, it was found that the stilbene based optical brightening agents can be used in combination of UV irradiation for the improvement of CIE whiteness value without compromising the fastness properties. In future study, the detailed structure elucidation will be performed using advanced spectroscopic techniques.

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