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Development of *p*H sensitive turmeric dyed fabrics for detection of acetic acid vapours

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A fabric sensitive to acidic vapors has been developed, using cationized cotton with eco-friendly *p*H-sensitive colorant turmeric. The fabric displays a color change in acidic and alkaline conditions on immersion and to acidic vapors. The fabrics show excellent reversibility on washing and can be used multiple times.

Keywords: Acidic vapors, Cationized fabric, Color change, *p*H sensing, Fabric reversibility, Turmeric dye

1 Introduction

Industrial pollution is one of the greatest challenges to mankind in this century. Pollution in the air is one of the serious threats, particularly when a person working in various industries has to face it in a day-to-day scenario. Among the various air pollutants, acidic vapor remnants emanating from the process of various industries cause significant impairment of sensory organs, apart from damage to internal organs upon prolonged exposure. Acetic acid vapors arising from industrial manufacture or domestic appliances could produce some irritation of eyes, nose, and throat and can result in damage of internal organs if exposed to greater than 100ppm (ref. 1). The personnel working in these industries are mostly unaware of the vapors emanating from the process until they face health issues. A color-based sensor would be useful to warn the personnel of the impending danger posed by acidic vapors. In industries, textile-based home furnishings can act as sensors and it will be useful for them to monitor the process and take remedial action. A lot of *p*H -sensitive dyes such as phenolphthalein, phenol red, methyl orange are used to monitor the *p*H of skin, sweat, urine, wound liquids, etc., along with textile substrates. However, an environment - friendly dye, which can be reversed back to its original color on washing, would be very apt for this application. Among the various dyes, turmeric exhibits these qualities and is found safe because of its non-toxic, non-allergic, and biodegradable nature. *Curcuma longa* L., collectively known as turmeric, is used as a colouring agent by food and textile industries (Natural Yellow 3, Color Index 75300-E100). The pigments in the extracts from rhizomes of *Curcuma longa* L., (Zingiberaceae) are curcuminoids and its main component is curcumin[2]. Curcumin is a hydrophobic polyphenol compound, which has a naturally yellow-orange color. Curcumin demonstrates keto-enol tautomerism; at basic medium, the enolate form is the prevailed form of curcumin and in the *p*H range of 3-7, Curcumin demonstrates the H-atom donor characteristic because of its keto form[3]. Recently, it has been reported that extracts from *Curcuma longa* L., have *p*H sensitivity in solution, showing different colours (from yellow to red), depending on the *p*H of the extracting solutions[4,5]. Curcuma and Curcuma-derived products have been applied onto textile materials as a dye and also as antifungal and antibacterial agents[6]. Another property of the Curcumin is that it can act as a *p*H-sensitive dye for sensors in contact with human skin apart from wound healing[7]. Moreover, curcumin is a food-derived product that will not produce health problems in case of leaching and is cost-effective. In this work, commercially derived colorant from *Curcuma longa* L. was used to dye cotton fabric and cationized cotton fabric. The interaction between cotton and turmeric colorant molecules involves weak intermolecular forces, such as van der Waals and hydrogen bonding, due to the enol structure of curcumin contained in Curcuma[7, 8]. The other challenge that needs to be addressed is the durability of natural colorants on textile substrates.

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Cationization of cotton is one of the effective ways to improve dye durability with excellent scalability at the industrial level. Hence, in this present work, it is planned to develop a *p*H-sensitive fabric sensor that can be used for acidic vapors using cationized cotton and cotton fabric. The efficiency of the cotton fabric and cationized cotton fabric was studied by exposing the fabric to various *p*H conditions and the color change was measured using a UV-Visible spectrophotometer. The reversibility of fabric was also studied and reported.

2 Materials and Methods

2.1 Materials

Cotton knitted fabric (RFD) of weight 180g/m^2 was procured from Kumaragiri Spinners Pvt. Ltd, Erode, India. 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC a cationic agent), which is commercially available as a 65% solution (65.4 w/w percentage in water), was procured from Sigma-Aldrich Pvt. Ltd, USA. Sodium chloride (NaCl), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) were procured from SRL Chemicals Pvt. Ltd, Mumbai, India. The extracts from rhizomes of *Curcuma longa* L. (Zingiberaceae) were powdered and used for the coloration process.

2.2 Methods

2.2.1 Cationization of Cotton Fabric

The cationization of cotton knitted fabric (10×10 cm) was carried out using an Infrared dyeing machine. The fabric was first treated with 20gpL of NaOH at room temperature (27°C) and the temperature was further raised to 80°C for 20 min. Following this, 80gpL of cationic agent (CHPTAC) was added to the bath and kept for 40 min. After cationization, the water was drained out, which was followed by a hot wash, cold wash, acetic wash until the fabric was neutralized [9].

2.2.2 Dyeing of Samples

Dyeing of control and cationized samples was carried out using turmeric as a colorant [10, 11]. IR dyeing machine was used for dyeing and the temperature of the bath was maintained at 50°C for 30 min followed by a hot wash, cold wash, and acetic wash[12]. The shade % of dyeing was fixed at 5%, 10% and 15% respectively. The samples were dried and stored in an airtight atmosphere.

2.2.3 Sensitivity of pH Sensor

The *p*H sensitivity of the fabric to acidic solution and vapors was tested. The fabric was immersed in the acetic acid solution for the dipping process, and in vapor it was placed above the acetic acid solution and tied tightly. The samples were dipped in the acetic acid solution for 5 min and taken for color measurements [13]. In the case of acidic vapors, the fabric was exposed to acetic acid vapors and after 48h they were taken for color measurements.

2.2.4 Color Parameters Studies

The dyed samples and the samples subjected to acidic treatment were characterized for color change using a HITACHI U-3210 UV-Visible spectrophotometer, Japan. The color parameters, namely *K*/*S*, RCS, CIE, L*a* and b*, were calculated as per the standard equations.

2.5 TGA Studies

Thermogravimetry analysis trials were performed for control, control dyed and cationized, cationized dyed fabric (10g) using a platinum crucible. The following conditions were deployed: sample mass 1mg, initial temperature 30°C, final temperature 700°C, heating rate 20°C/min and nitrogen 50 mL/min (purging gas).

3 Results and Discussion

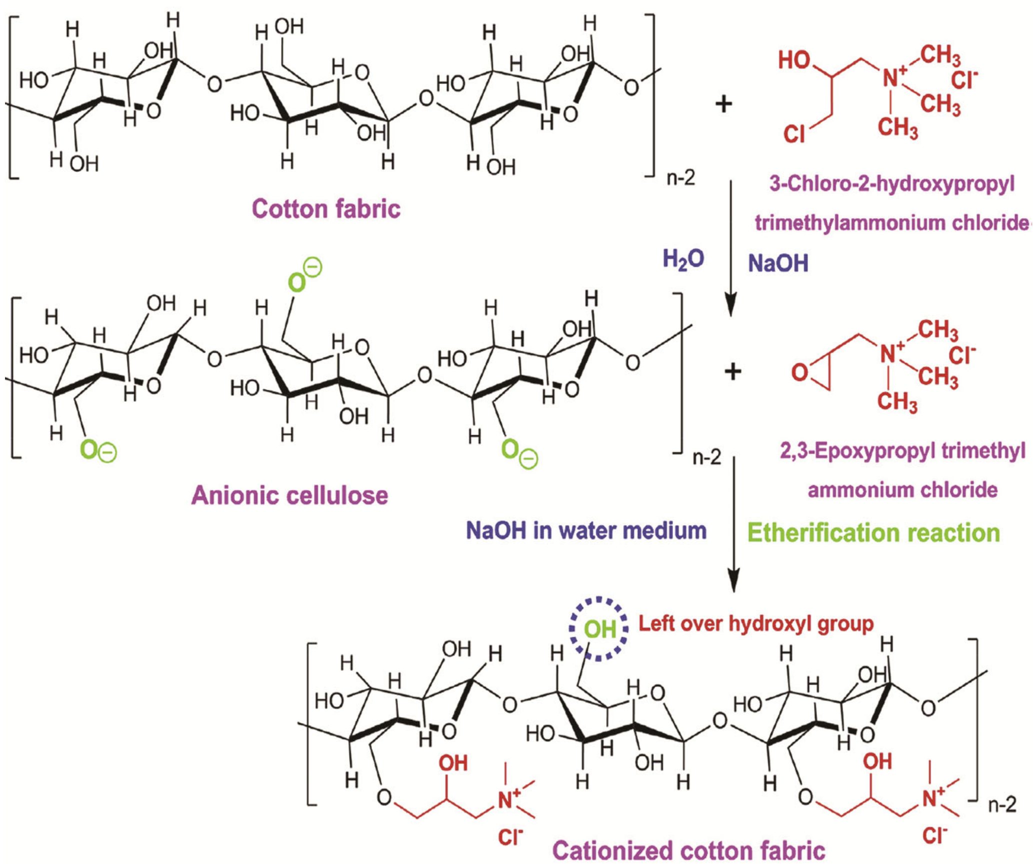
3.1 Color Measurements Studies

The control fabrics and cationized fabrics are dyed at varying concentration (5%, 10%, 15% shade) using turmeric as a colorant. The reaction of cationizing agent to that of cotton fabric is given in Scheme 1 [9]. The reflectance curves of the samples are given in Fig. 1. The L* value which is lighter or darker, a* value which denotes redder or greener and b* value which denotes yellower or bluer color are significantly altered upon cationization. Comparison of L* (Table 1) shows that the cationized samples are darker as compared to the control, whereas the increase in a* values of the cationized sample shows that the sample becomes redder. The decrease in b* values for cationized samples shows that the fabric is less yellower[14, 15]. The relative color strength (RCS) of control and cationized samples is also shown in Table 1.

It can be seen that 204 %, 285 % and 270% increase in color strength is achieved for cationized samples of 5%, 10% and 15% shade. The improvement of RCS can be attributed to better binding of the dye to the substrate. The reaction molecule of dye to the cationized fabric is given in the reaction Scheme 1 [9].

3.2 TGA Analysis

The TGA profiles of various fabrics taken for the TGA study is given in Fig. 2. It can be seen that a slight improvement in thermal properties is observed



Scheme 1 — Reaction mechanism for cationized cotton fabric

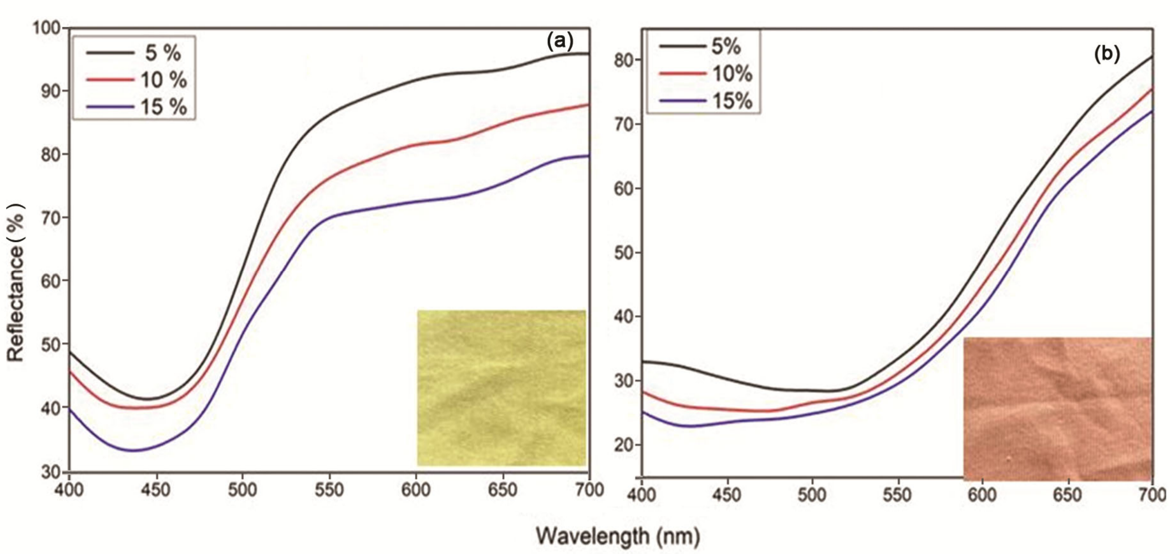


Fig. 1 — Reflectance curve (a) control fabric and (b) cationized fabric

for cationized samples. However, on dyeing, the fabric curves are shifted towards the lower temperature. The thermal profiles reveal that the cationization does not affect the temperature resistance of the fabric [15].

3.3 SEM Analysis

The SEM images of various fabrics are given in Fig. 3**.** The cotton fibres in the fabric have convoluted morphology, which is the characteristic feature of cellulosic materials. The fibres in the cationized fabric show little rounded rod-like morphology due to the addition of alkali during the cationization process [16].

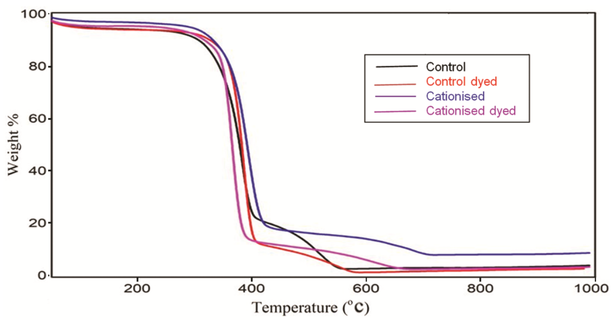


Fig. 2 — Thermogravimetry analysis

3.4 FTIR Analysis

Figure 4 shows the characteristic cellulosic peak at 1017 cm^{-1}, due to strong absorption peak for –OH stretching at 3313 cm^{-}1, C–H stretching at 2889 cm^{-1} and C–O stretching vibration at 1017 cm^{-1} (ref. 17). Compared to cotton fabric, cationized cotton has a new peak at 1200cm^{-1}, which corresponds to presence of cellulose. A sharp peak at 1491 cm^{-1} corresponds to the presence of quaternary ammonium (3R–N+ –)[18, 19] groups. These peaks confirm the fixation of CHPTAC on the cotton fabric. The peak at 1147 cm^{-1} corresponds to the C–O stretch of phenyl alkyl ether and it confirms the presence and attachment of turmeric colorant on fabric [20].

3.5 *p*H Testing Sensor

To test the effectiveness of the developed samples across various *p*H, 15% shade fabric is subjected to *p*H 5, 7 and 9. The values of *K*/*S* and L*, a*, b* after subjecting to various *p*H conditions are given in Table 2 and the reflectance curves are given in Figs 5(a) & (b). It is evident that the control sample is yellower in color but on treating the sample at acidic condition, there is no significant change in color,

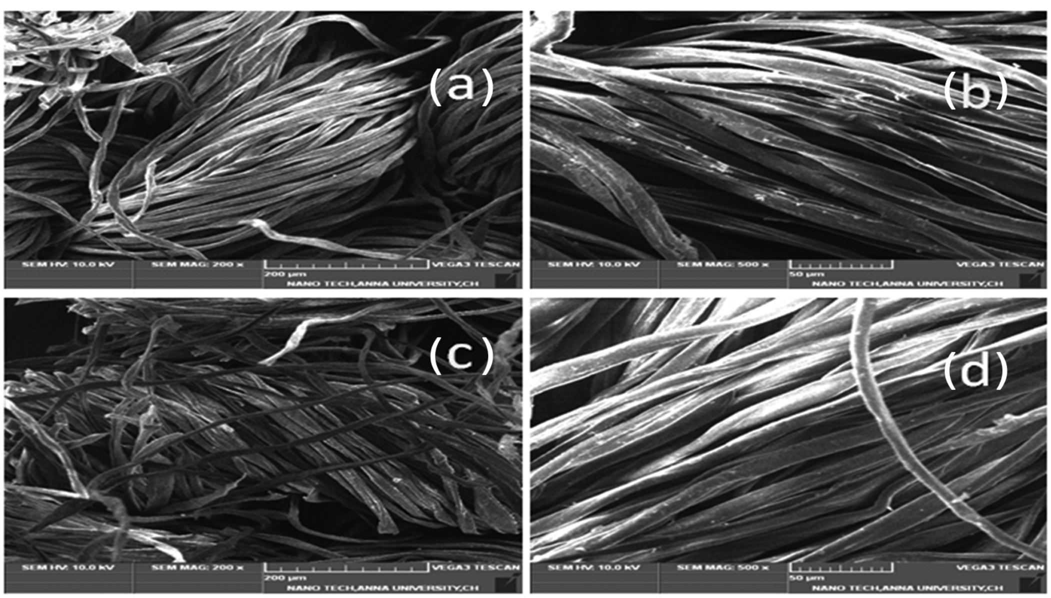


Fig. 3 — SEM images (a) control, (b) control dyed, (c) cationized and (d) cationized dyed fabrics

Table 1 — CIE L*a*b* values of control and cationized fabrics

% shade	Control fabric				Cationized fabric				RCS, %
	L*	a*	b*	K/S	L*	a*	b*	K/S	
5	93.26	4.16	39.89	0.45	67.96	26.29	14.54	0.92	204
10	89.08	5.16	35.01	0.42	65.86	23.63	17.69	1.20	285
15	82.87	14.77	31.63	0.47	66.62	22.28	12.17	1.28	270

whereas while subjecting the fabric to alkaline condition, the sample becomes redder which is evident by the increase in a* values, and decrease in b* values.

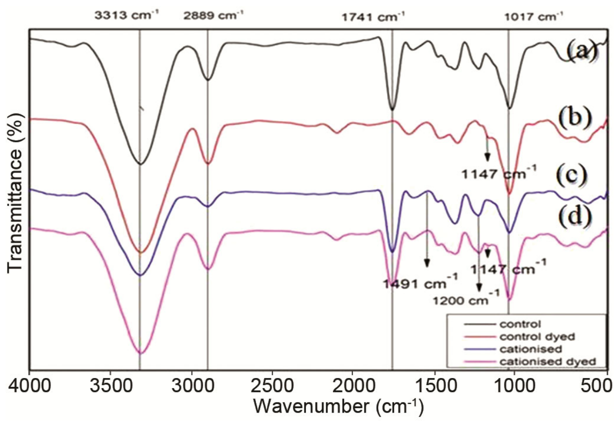


Fig 4 — FTIR spectra of (a) control (b) control dyed, (c) cationized and (d) cationized dyed fabrics

The sensitivity of fabric to alkaline condition is due to curcumin which demonstrates keto-enol tautomerism. At basic medium, the enolate form is the most prevailed form of curcumin. In the *p*H range of 3-7, curcumin exhibits the H-atom donor characteristics because of its keto form[3] and is explained in reaction Scheme 2.

In the case of cationized samples, the fabric becomes yellow from being redder in color. The increase in b* values and decrease in a* values confirm the change. Moreover, the sample becomes lighter in color with the increase in L* values. The

Table 2 — CIE L*a*b* values of *p*H exposed fabrics

*p*H	Control fabric			Cationized fabric		
	L*	a *	b *	L*	a *	b *
5	83.46	8.07	69.73	79.32	10.49	50.47
7	75.09	9.16	21.05	66.33	35.06	14.13
9	69.73	54.16	14.93	76.21	39.10	12.20

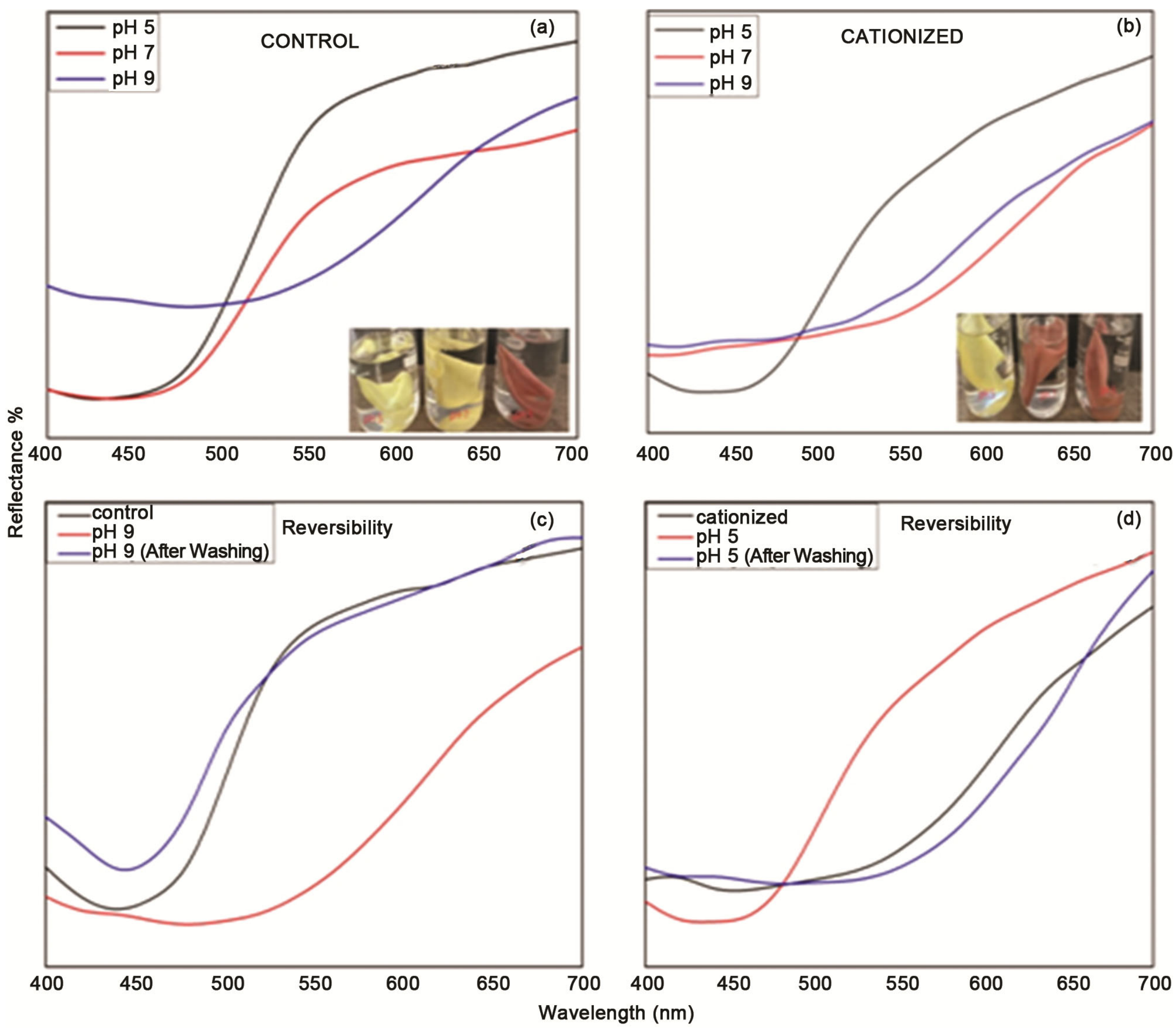
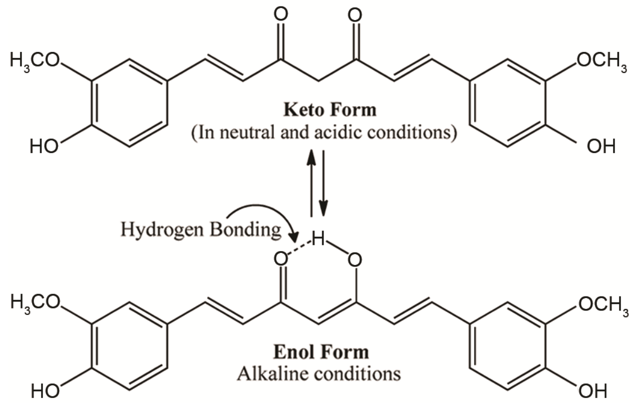


Fig. 5 — Reflectance curves (a) control, (b) cationized fabric, (c) control reversibility and (d) cationized reversibility



Scheme 2 — Chemical structure of turmeric at enol and keto forms

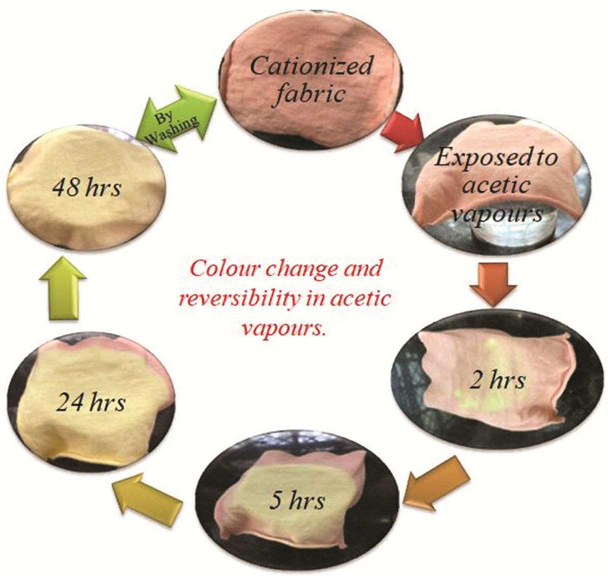


Fig. 6 — Reversibility of cationized fabric

reversibility of the fabric is also studied by washing the fabric. Figs 5 (c) & (d) show the reflectance curves after washing of control and cationized fabrics.

From Table 3, it is evident that the color change occurs prominently in the alkali medium for control samples and in the acidic medium for cationized samples. After washing, sample retains almost the original color before subjecting to *p*H treatment and this is evident from the reflectance curves of CIE, L*a*b* values.

3.6 Acetic Vapors

In normal industrial practice, the vapors are likely to emanate, and hence the sensitivity of the fabric to vapors is also studied. The images of sample subjected to acetic acid vapors are shown in Fig. 6. and Color parameters values indicate that the cationized fabric subjected to acetic acid vapors changes to yellow, as given in Table 4.

The increase in b* values confirms that the fabric is sensitive to acidic vapors and the decrease in a* value confirms the same. The color changed fabrics upon treatment with water reversed back to the original color. The cationized fabric can be used as a sensor to warn the industry personnel working in an acidic environment (Fig 6.**)** However, the control fabric shows no change in acidic vapor conditions.

4 Conclusion

In Industry, where acidic vapours are emanating, a *p*H sensitive textile upholstery is likely to provide a warning signal. In the present work, a *p*H sensitive fabric dyed with turmeric colorant has been developed using cationized cotton. The developed fabrics are tested for its sensitivity in acidic and alkaline solutions. In addition to that, the fabrics are tested against acidic vapours. The fabrics upon exposure to solutions of varying *p*H exhibit change in colour with reversibility upon washing. The cationized fabrics show high sensitivity to acidic vapours as compared to control cotton fabrics. Moreover, the cationic agent has ensured excellent fixation of dyes onto fabric, thereby enhancing the durability of fabrics.

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