

Fabrics dyeing with colorimetric pH-responsive colors

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Abstract

Textiles with halochromic properties are having a significant attention due to their flexibility, mechanical properties, lightweight and washability. These properties allow to produce wearable pH sensitive devices, that might be employed in a wide range of applications. The manuscript shows the possibility to dye textiles fabrics with halochromic dyes. Five different halochromic dyes were tested; Bromocresol purple, m-Cresol purple, Chlorophenol red, Curcumin and Bromothymol blue. The dyeing recipe was applied on a multifibers textile fabric to test the affinity of the different fibers for the dyes. The multifibers fabric was composed of wool, polyacrylonitrile, polyester, polyamide 6.6, cotton and cellulose acetate. The dyes were solubilized in a water solution and the dyeing process was carried out with no auxiliaries added into the dyeing liquor. Only temperature and time were the key parameters. On the dyed fabrics washing and light fastness were evaluated as well as colour changing at different pH. Some fibers, polyamide 6.6 and wool in particular, showed good dye fastness and halochromic properties. Bromothymol blue was selected to dye polyamide 6.6 and cotton fabrics. Cotton required a mordant application step before the dyeing. Both cotton and polyamide 6.6 evidenced good halochromic properties in a pH range from 4 to 10. Cotton fabrics exhibited an immediate color changing; polyamide 6.6 changed colour after few minutes; heat accelerated the process. On the other hand cotton fabrics showed a poor light and washing fastness while polyamide 6.6 evidenced a good dye fastness. An industrial dyeing process was performed on natural cellulosic

25 fibers. The results confirmed the possibility for a scale-up of the process in view of textile disposable
26 applications.

27

28 *Keywords:* Dyeing, , Halochromic Dyes, Dye fastness, Textiles

29 **1. Introduction**

30 Recent literature reported an increasing number of papers related to pH-sensitive materials or devices
31 [1-5]. Wearable technologies can offer the opportunity of continuous monitoring of the health status.

32 The real time check of physiological parameters (including pH of sweat) is growing among athletes
33 and the medical community, for instance. In fact, sweat is a good option to collect information about
34 the physiological status of a subject [6]. In addition, the pH of the skin plays a role in the development
35 of skin disorders such as infections and dermatitis [7]. Moreover, a pH-sensitive wound dressing can
36 indicate the progress of healing by a simple colour observation.

37 pH sensing for healthcare applications (wound monitoring, implantable or wearable devices) requires
38 materials with high level of bio-compatibility, sensitivity, reproducibility of the results and stability
39 to mechanical stresses combined with low-cost fabrication technologies [8,9]. Textile materials are
40 the substrates of choice for developing wearable devices because of mechanical properties, flexibility,
41 breathability, lightweight and washability. Furthermore, textile materials can cover large surfaces,
42 but if the whole surfaces is sensitive, a single spot of pH variation can be detected [10]. Besides, a
43 pH-sensitive textile might be used in many industrial applications, like filtration, storage of perishable
44 goods (e.g. food) and protective clothing.

45 On the other hand, colorimetric pH-responsive materials are largely favourite to develop cheap
46 technologies because of the lack of electrical components and simplicity of the design. In addition,
47 there are no needs for complex equipment and skilled personnel for the result interpretation.

48 Halochromic properties of a dye can be affected by the matrix as a result of polar interactions between
49 the dye molecules and the nearby chemical groups of the matrix [11, 12,13].

50 Halochromic dyes have been used to produce pH-sensitive fabrics and fibers using conventional
51 dyeing or unconventional processes, such as sol-gel, encapsulation and electrospinning [14]. In
52 particular, Methyl Red was applied on bleached cotton, polyamide 6.6 6 and polyamide 6.6 fabrics
53 using both a conventional dyeing process and a sol-gel technique [15]. Conventional dyeing resulted
54 in an uneven and not stable dyeing on cotton fabrics, while good coloration was obtained on
55 polyamide 6.6. Sol-gel technique provided a good and stable colour on cotton and polyamide 6.6s.
56 Moreover, fabrics treated with sol-gel showed faster colour changes related to pH compared to
57 conventional dyed fabrics. In addition, the halochromic performance using the sol-gel technique is
58 not greatly affected by the matrix.

59 Cotton fabrics modified with *N,N'*-methylenebisacrylamide were dyed with bromothymol blue [16].
60 Two pH indicator dyes (Brilliant Yellow and Alizarin) were used to dye cotton and polyamide 6.6s
61 after a selection between several halochromic dyes [17]. The fabrics showed halochromic properties
62 with slow colour transitions from a colour to another in the order of half an hour to about 2 h.

63 Brilliant Yellow and Congo Red were used to print poly(ethylene terephthalate) fabrics using a
64 plasma-assisted sol-gel method [18]. The procedure involved five main steps: 1) treatment with an
65 oxygen plasma under vacuum; 2) padding in a sol of 3-propylaminotriethoxysilane (precursor) and
66 ammonium hydroxide (catalyst) in ethanol and water; 3) air-drying; 4) post-treatment either thermally
67 in a convection oven (pad-dry-cure method) or by oxygen plasma; 5) flat screen-printing of a paste
68 containing the halochromic dye. The printed fabrics showed slight changes in colour from pH 4 to 8
69 when Brilliant Yellow was used, while printing with Congo Red showed a blue colour at pH 3 and
70 red at pH 6.

71 In a study, Nitrazine yellow was applied to fabrics of polyamide 6.6s (6 and 6.6) using a conventional
72 acid dyeing process; as well as polyamide 6.6 6 and polyamide 6.6 nanofibers mats were produced
73 by electrospinning using a certain amount of the dye in the polymer solution [19]. Both fabrics and
74 nanofiber mats were treated with poly(diallyldimethylammonium chloride) as a complexing agent to
75 fix the dye. The fabrics showed a reversible colour changes from yellow to blue in a broad range from

76 pH 3 to 10 with a maximum responding time of 20 min. The electrospun mats showed a similar
77 behaviour, but colour transition was faster with a response within 5 min. The results demonstrated
78 that the matrix and the shape of the fibrous structure can affect the halochromic properties in
79 broadening the pH of colour transition, changing the hue of the dye, and altering the response time.
80 The same methods (i.e. conventional dyeing of fabrics and dye-containing nanofibers by
81 electrospinning) was followed using sulfonphthaleine dyes with different substituents on polyamide
82 6.6 matrix [20]. The substituents greatly affect both stability and halochromic properties of fabrics
83 dyed with conventional dyeing process. A linear correlation was found between the molecular
84 weights and the dye leaching. In electrospinning, strong acid conditions improve the stability of the
85 dyes in the matrix. Moreover, a polycation enhanced the stability of the dyes with bromine
86 substituents.

87 Recently, a fast-responsive colour transition was reported on micro-fibrillated cellulose sponges
88 loaded with tricyanofuran hydrazine synthesized from 4-aminobenzonitrile and tricyanofuran [21].
89 The sponges showed an instantaneous colour shift from yellow to orange, red or blue depending on
90 the pH of the solution. The coloration of the sponges resulted completely reversible to pH and highly
91 stable to several cycles.

92 Some natural dyes exhibit halochromic properties too. Curcuma powder from *Curcuma longa* L. was
93 used to dye polyamide 6.6 and cotton fabrics [22].

94 Recently, anthocyanins extracted from purple sweet potato were used to dye silk fabrics. The colour
95 of the fabric quickly changed from red-pink to purple, blue and green as the pH value increases from
96 2 to 10 [23]. Anthocyanins extracted from purple sweet potato were also added to electrospinning
97 solutions of polyvinyl alcohol and sodium alginate mixture at different concentrations to produce
98 electrospun nanofibers mats with halochromic properties [24]. The resulting nanofiber mats changed
99 colour in about 10 s from pink at pH 4-6 to green at pH 8-10.

100 Finally, Bromothymol blue was grafted to cellulose modified with hydroxypropyltriethylamine
101 groups in order to obtain pH-sensitive fibers [25] and films [26].

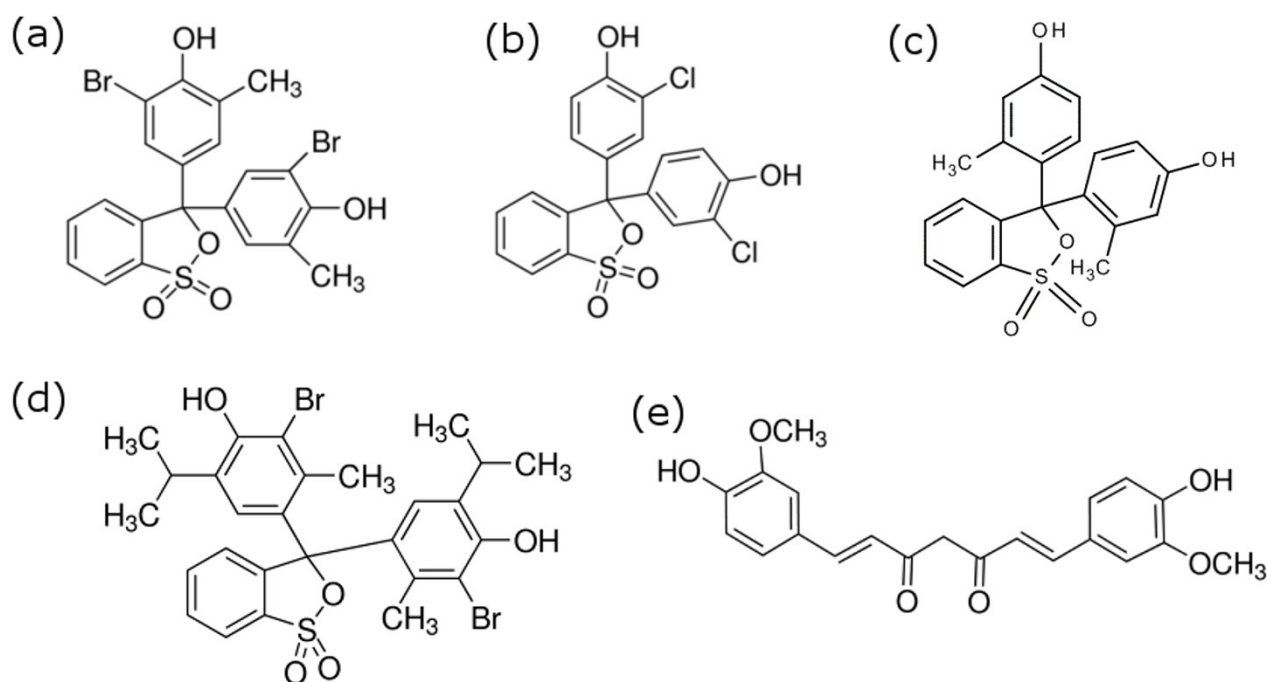
102 In this work, five halochromic dyes were selected to dye a multifibers textile fabric composed of wool,
103 acrylic, polyester, polyamide 6.6, cotton and cellulose acetate strips. The multifiber textile substrate
104 was employed to have a screening on fibers affinity for the dye. Bromothymol blue was chosen as
105 the dye and among the fibers tested, polyamide 6.6 and cotton were selected to dye larger fabrics as
106 well as knitted cotton fabrics normally used as medical gauze. An industrial trial was performed at
107 Tintoria Finissaggio 2000 s.r.l. on a cotton gauze and on a linen woven fabric.

108

109 2. Experimental

110 2.1 Materials

111 Five halochromic dyes were employed. They were supplied from Aldrich and used as received. In
112 figure 1 their respective chemical formula are reported.



113

114 **Fig. 1** Chemical structures of the halochromic dyes employed: a) Bromocresol purple;

115 b) chlorophenol red; c) m-Cresol purple; d) Bromothymol blue; e) Curcumin

116 The multifibers textile fabric was supplied from Ausiliari Tessili (Italy). It is composed of wool,
117 polyacrylonitrile (acrylic), polyester, polyamide 6.6, cotton and cellulose acetate (acetate) bands. The

118 standard PA 6.6 textile fabric (124 g/m²) was purchased from Ausiliari Tessili as well. The knitted
119 cotton gauze (74 g/m²) was kindly offered by Yanga s.r.l. (Italy). The dyed knitted elastic cotton
120 gauze (184 g/m²) and the linen textile fabric (160 g/m²) were granted by Tintoria & Finissaggio 2000
121 (Italy). Neofix E-117/B (polyethylene-polyamine cationic resin) was kindly supplied by Tintoria
122 Finissaggio 2000 s.r.l., Albegal levelling agent was purchased from Huntsman Italia S.r.l. (Italy).

123 *2.2 Methods*

124 *2.2.1 Laboratory Dyeing*

125 Rectangles of multifibers textile fabric having a size of 5 by 15 cm were cut and dyed according to
126 the following conditions; liquor ratio 1:20 (10 g of textile material in 200 ml bath); temperature 100°C
127 with a heating rate 1°C/min; process temperature and time 100°C 40 min. Dyes concentration 1 g/L.
128 The dyeing process was carried out in an AHIBA Nuance Top Speed II equipment. Speed was 35
129 rpm and reverse time 3 min.

130 The dye Bromothymol blue was selected to dye different textile fabrics; a standard Polyamide 6.6
131 and a cotton gauze.

132 Polyamide 6.6 was dyed according to the same conditions as reported for multifibers textile fabric.
133 The cotton gauze was scoured in sodium hydroxide solution (2% w/v) at 90°C for 1 h under stirring.
134 Before the dyeing process the gauze was immersed in a 2% (w/v) acetic acid water solution and 3%
135 (w/v) Neofix E117/B was added as dye fixing agent. The textile was soaked in the solution and left
136 for 20 min at 60°C. It was subsequently rinsed in cold water for 20 min. After this step the dyeing
137 process was carried out. In the dyeing liquor 2% (w/v) acetic acid and 2% (w/v) Albegal were added.

138 *2.2.2 Industrial Dyeing*

139 The knitted cotton and the linen textile fabric were dyed at Tintoria Finissaggio 2000 s.r.l.

140 *2.2.2.1 Knitted cotton fabric dyeing*

141 A scouring phase before the dyeing process was performed. 9 kg of knitted fabric were soaked in 600
142 L bath; sodium hydroxide and hydrogen peroxide were employed. Temperature was set at 98°C for

143 40 min. Following this step the mordant phase was carried out in Neofix E117/B water solution at
144 60 °C for 20 min. The dyeing process was carried out at 100°C for 45 min. Bromothymol blue was
145 selected and used in 1% concentration. Process conditions were the same as those of the laboratory
146 dyeing. Afterward the textile substrate was rinsed in cold water and dried at 120°C.

147

148 *2.2.2.2 Linen fabric dyeing*

149 Before the dyeing a pre-scouring and a scouring step were carried out. 16 kg of fabric were dipped in
150 600 L bath with antifoaming and soaking agents in an oxalic acid water solution at 60°C for 20 min,
151 subsequently the fabric was rinsed in cold water and immersed in a sodium carbonate solution at 40°C
152 for 10 min and then rinsed again in cold water. The scouring as well as the mordant phase of the
153 textile material were performed at the same conditions described for cotton. For the dyeing process
154 Bromothymol blue in concentration 1% was selected and the process conditions maintained as those
155 of the laboratory experiments.

156 *2.3 Analysis*

157 *2.3.1 Washing and dry-cleaning fastness*

158 Washing fastness of the dyed textile fabrics was evaluated according to standard ISO 105-C06. ECE
159 detergent from EMPA test material was in 4 g/L concentration, temperature was raised at 40°C and
160 left for 30 min.

161 Standard ISO 105-D01 was employed for dry cleaning fastness. The fabrics were soaked in
162 Tetrachloroethylene, from Riedel de Haën. Temperature was set at 30 °C for 30 min.

163 *2.3.2 Light fastness*

164 The light fastness of the dyed fabrics was evaluated by means of a XENOTEST ALPHA apparatus
165 equipped with a Xenon lamp according to standard ISO 105. The dyed fabrics were exposed to the
166 artificial light under controlled conditions with a set of reference materials. The color fastness is
167 assessed by comparing the change in color of the test specimen with that of the reference material

168 used. The reference material is composed of blue dyed wool textiles with a known reaction to light.
169 They range from 1 (very low color fastness to light) to 8 (very high color fastness to light).

170

171 2.3.3 Halochromic test

172 In the halochromic test the dyed fabrics were dipped in solutions having pH from 4 to 10. pH 4; 7 and
173 10 were buffered solution from Fluka. Other pH range were prepared according to table 1.

174

175 **Table 1.** Buffer solutions compositions

pH	Buffer components		Composition (% vol.)		
	A	B	A	B	Distilled water
5.5	0.1 N sodium acetate	0.1 N acetic acid	11.0	89.0	-
6.2	0.2 M imidazole	0.1 N HCl	25.0	43.4	31.6
6.6			25.0	36.5	38.5
7.4			25.0	10.2	64.8
8.0	0.1 M glycine in 0.1 M NaCl	0.1 N NaOH	98.7	1.3	-
8.5			94.7	5.3	-
9.3			84.0	16.0	-

176

177 2.3.4 UV-Vis analysis

178 UV-Vis analysis was carried out by means of a Perkin Elmer UV-Vis spectrophotometer λ 35. The
179 dyes solutions were analysed in a wavelengths range from 400 to 700 nm, with a data interval 1 nm.

180 2.3.5 Colorimetric analysis

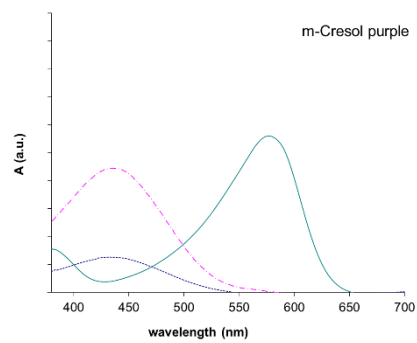
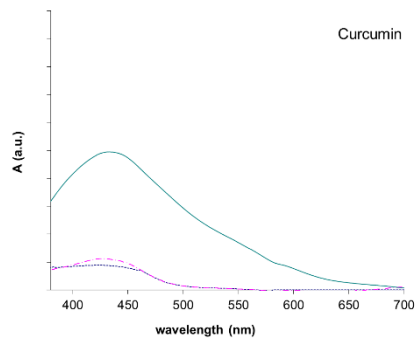
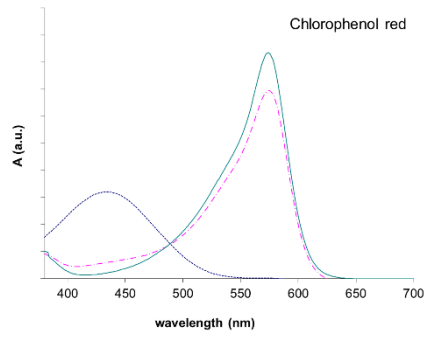
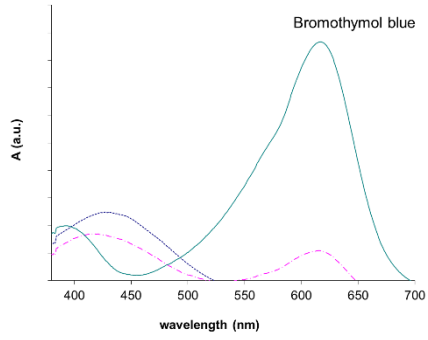
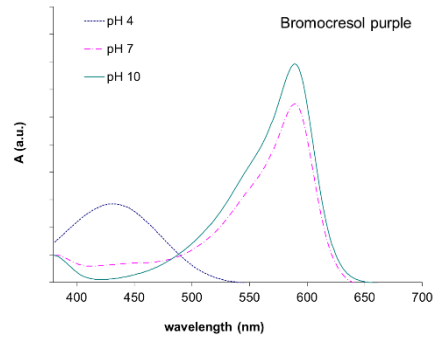
181 Colorimetric analysis were performed with a Datacolor SF 600 X spectralflash with CIE standard
182 illuminant D65, 10 deg. The CIElab colorimetric coordinates of the tested samples were registered.
183 Five measurements for each sample were performed and the mean value was reported.

184 3. Results and discussions

185 3.1 Evaluation of the halochromic properties of the dyes

186 Five solutions with 1 g/L concentrations were prepared for each dye subsequently employed in the
187 dyeing process. The solutions were prepared in water and magnetically stirred at 50°C for 30 min to
188 favour the solubilization of the dyes. Curcumin is a polyphenolic compound insoluble in water in
189 acidic and neutral pH conditions. To improve its solubility 30% v/v ethanol was added. The prepared

190 solutions were then dilute 1:100 in different buffered solutions at pH 4, 7 and 10. The UV-Vis analysis
191 of the solutions are reported in fig. 2.



193 **Fig. 2** UV-Vis analysis of the dyes solutions prepared in different buffered solutions at pH 4; pH 7
194 and pH 10
195

196 The analysis performed evidenced different wavelengths of absorption changing the pH of the
197 solutions. In acidic condition, at pH 4, all the dyes analysed show an absorption peak at wavelength
198 400-450 nm corresponding to the violet-blue wavelength of absorption, so as the perceived color of
199 the solution is yellow. Bromocresol purple and chlorophenol red display a shift in the absorption peak
200 at higher wavelengths by increasing the pH of the solutions at 7 and 10, corresponding to the yellow
201 absorption wavelength at 590-600 nm. The color of the solutions turned into purple-violet. In *m*-
202 cresol red spectra a shift of the absorption peak is visible at pH 10, from 450 nm to 580 nm so as at
203 pH 10 the solution is purple. Bromothymol blue evidence a wider shift in the absorption peak by
204 changing the pH of the solutions. At pH 7 and pH 10 the shift of the absorption peak moves from 650
205 to 680 nm and the solutions change their colors from violet-blue to blue-green. According to *de Meyer*
206 *et al.* the color change of the dye solutions is due to a protonation/deprotonation mechanism that
207 causes a different electron configuration resulting in a different interaction with the visible light. The
208 dyes analysed, apart from Curcumin, belong to the class of sulfonphthalein dyes, where the color
209 change is due to the ring-opening reaction as a consequence of deprotonation. A scheme of the
210 reaction is reported in fig. 3.

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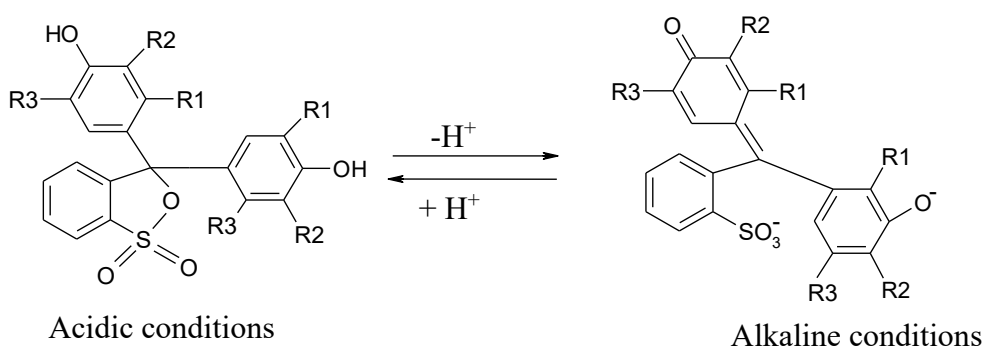
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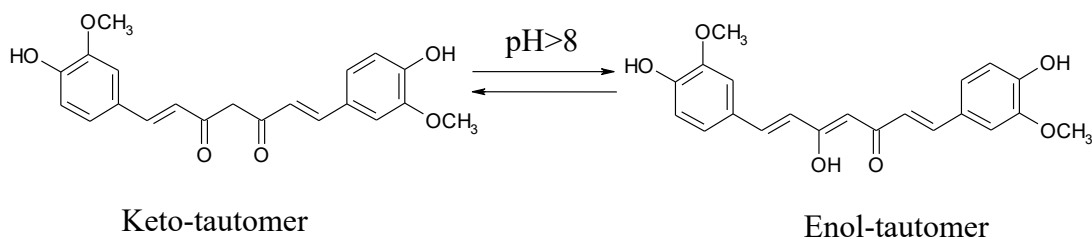
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217 **Fig. 3** reaction scheme of the sulfonphthalein dyes in acidic and alkaline conditions

218

219 Curcumin, bis- α,β -unsaturated β -diketone or diferuloylmethane, is a compound which exhibits *keto-*
 220 *enol* tautomerism. Fig. 2 evidences that in acidic and neutral medium Curcumin spectra indicates a
 221 yellow solution belonging to the *keto* form while in alkaline conditions evidences a chromatic change
 222 to red due to the *enol* form: at pH 10 it is clearly visible a wider peak of absorption that covers the
 223 range of red/brown color. In figure 4 the scheme of reaction is reported.



228 **Fig. 4** scheme of the structural changes in curcumin molecule in acidic and alkaline conditions

229

230 3.2 Multifibers textile fabric dyeing

231 The dyeing process performed on the multifiber textile fabric evidenced that halochromic dyes can
 232 be successfully incorporated in some textile materials with a conventional dyeing method, simple and
 233 low cost, in which only temperature and time are the key process parameters, with the addition of no
 234 dyeing auxiliaries.

235 In the process conditions adopted the dyes showed excellent affinity for wool and polyamide 6.6
 236 fibers; poor affinity for cotton and acetate and no affinity for the other fibers (acrylic and polyester).

237 Only curcumin evidenced affinity for all the fibers. In fig. 5 the results of the dyeing process are
 238 reported.

239



243 **Fig. 5** results of the dyeing process on the multifibers textile fabric; A) -Bromocresol purple;

244 B) -Curcumin; C) -*m*- cresol purple; D) -Chlorophenol red; E) - Bromothymol blue

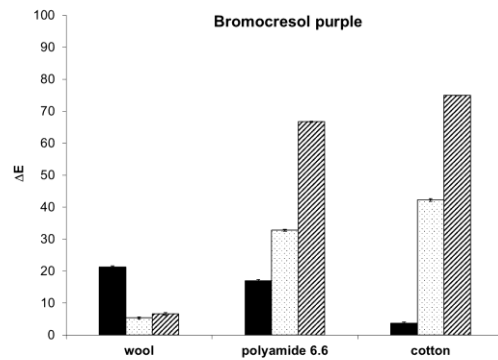
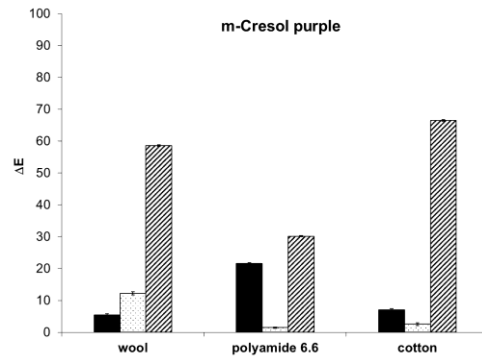
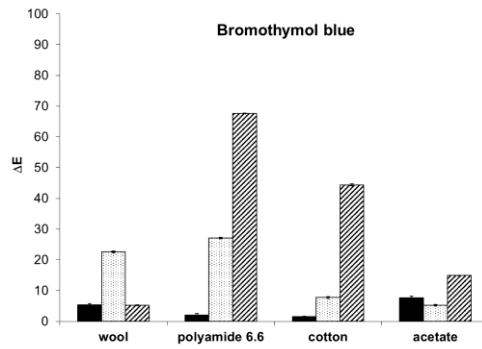
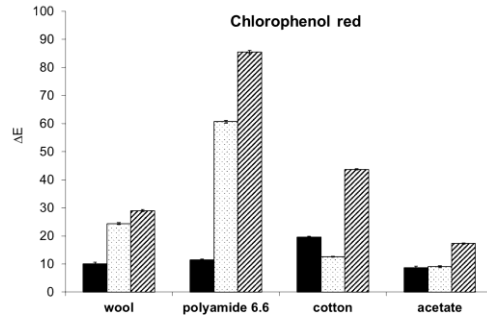
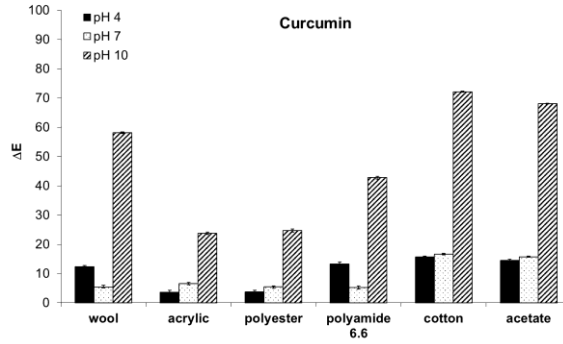
245 Since no auxiliaries were added to the dyeing liquor, the slightly acidic conditions of the dyes
246 solutions, favoured the dyeing of fibers that require acidic conditions like wool and polyamide 6.6.
247 For their hydrophobic nature and low swelling in water solutions polyester and acrylic fibers showed
248 no affinity for the dyes at 100 °C with 40 min contact time. In addition the water solubility of the
249 dyes prevented the dye adsorption on the fibers. Cotton and acetate evidenced a very slight affinity.
250 This is probably due to a poor adsorption of the dye on the fibers as a consequence of the hydroxyl
251 groups acetylation of cellulose in the acetate fibers, as well as an incomplete reaction between dyes
252 and fibers for cotton. Moreover the good affinity of the dyes for wool and polyamide 6.6 decreased
253 the amount of dye accessible.

254

255 *32.1 Halochromic test*

256 The dyed multifibers textile fabrics were dipped in different buffered solutions at pH 4; pH 7 and pH
257 10. After drying them in oven at 50°C for 1 h, Datacolor analysis was performed on the fibers strips.
258 Figure 6 plots the CIElab ΔE values versus pH for each dye employed on the different fibers type.

259



261 **Fig. 6** ΔE against pH for each dye and fibers

262 The CIElab ΔE values were calculated according to eq. 1:

263
$$\Delta E = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2}$$
 eq. 1

264 Where L_0 ; a_0 ; b_0 are the colorimetric parameters of the reference sample according to CIElab color
265 space; L is the lightness value from black ($L = 0$) to white ($L = 100$), a is the value from green
266 (negative) to red (positive) and b is the value from blue (negative values) to yellow (positive values).

267 In the analysis performed L_0 ; a_0 ; b_0 where those of the dyed samples as obtained after the dyeing
268 process. L , a and b are those of the samples after immersion in the buffered solutions. General
269 considerations can be done about all the dyes analysed. Firstly the results obtained confirm that the
270 halochromism is maintained when the dyes are adsorbed on the fibers, in particular they showed a
271 color change in a pH interval around 7 and 10. Polyamide 6.6 and cotton are the fibers that evidenced
272 major ΔE values, easily detectable by naked eyes. Acetate fibers were characterized by low ΔE values
273 because a very low amount of dye was adsorbed on the acetate strip. Cotton evidenced a low amount
274 of dye after the dyeing process as well but color change was clearly visible at alkaline pH. Wool
275 evidenced a good dye adsorption but poor halochromic properties. Halochromism was appreciable
276 only with curcumin and m-Cresol purple at pH 10. As expected curcumin showed a visible color
277 change in the alkaline range as a confirmation of what was stated at paragraph 3.1.

278 *3.2.2 Dye fastness*

279 Washing and light fastness of the dyed fabrics were evaluated. Table 2 reports the results of the
280 washing fastness and table 3 of light fastness. According to the values assigned in the table, wool and
281 polyamide 6.6 manifested a good washing fastness for all the dyes while cotton and acetate evidenced
282 a very poor one. They show that the limited amount of dye adsorbed during the dyeing process was
283 barely adhered to the fibers.

284

285 **Table 2** Washing fastness of the dyes according to grey scale ISO 105 A02*

Washing fastness

Fibers type	Bromocresol purple	<i>m</i> - Cresol purple	Chlorophenol red	Bromothymol blue	Curcumin
Wool	4	5	4	4	4
Polyamide 6.6	5	5	4	5	5
Cotton	1	1	1	1	2
acetate	1	1	1	1	2

286 *the grey scale covers a range from 1 to 5; 5 represents excellent washing fastness, 1 very poor
287 fastness

288

289 As far as light fastness is concerned cotton and acetate evidenced a very low light fastness (rating 1
290 is the lowest value of the scale) confirming that the photosensitive dyes molecules are adsorbed only
291 on the surfaces of the fibers. Wool and polyamide 6.6 showed good light fastness. The best light
292 fastness was obtained on polyamide 6.6 dyed with bromothymol blue.

293

294 **Table 3** Light fastness of the dyes according to reference textile materials ISO 105-B02

light fastness					
Fibers types	Bromocresol purple	<i>m</i> - Cresol purple	Chlorophenol red	Bromothymol blue	Curcumin
Wool	3	2/3	2/3	2	2
Polyamide 6.6	2	2/3	2	3/4	1
Cotton	1	1	1	1	1
acetate	1	1	1	1	1

295

296 *3.3 Polyamide 6.6 textile fabric dyeing with Bromothymol blue*

297 Bromothymol blue was selected to dye polyamide 6.6 standard textile fabrics. Good results were
298 reached in the dyeing process and the fabric appeared to have a deep yellow color. Washing and light
299 fastness of the dyed fabric were evaluated. The results are shown in table 4. They confirm the data
300 obtained for multifibers textile fabric dyeing. Bromothymol blue evidenced an excellent washing and
301 light fastness on Polyamide 6.6 dyed at 100°C for 40 min with a 1 g/L dye concentration.

302 **Table 4** Washing and light fastness of the dyed polyamide 6.6

		Washing fastness	Light fastness
Bromothymol	blue	5	4
dyed Polyamide 6.6			

303

304 To evaluate the halochromic properties different portions of the dyed fabric were selectively dipped
 305 in the buffered solution at pH 4; pH 7 and pH 10. The CIElab colorimetric coordinates of the fabrics
 306 were subsequently evaluated. They are reported in table 5

307
 308
 309
 310
 311

Table 5 Colorimetric coordinates of the dyed polyamide 6.6 after immersion in buffered solutions at pH 4; 7 and 10

pH	T (°C)	L	a	b	ΔE
4	25	65.78 ± 0.62	34.36 ± 0.96	81.11 ± 0.77	7.12 ± 0.81
	50	66.64 ± 0.59	32.88 ± 0.46	82.05 ± 0.93	7.58 ± 0.70
7	25	55.84 ± 0.85	14.52 ± 0.51	64.44 ± 0.42	26.32 ± 0.63
	50	54.37 ± 0.67	10.17 ± 0.68	60.84 ± 0.93	24.56 ± 0.82
10	25	42.45 ± 0.92	-7.96 ± 0.88	40.65 ± 0.76	60.55 ± 0.92
	50	39.53 ± 0.51	-11.69 ± 0.67	34.50 ± 0.92	58.63 ± 0.82

312

313 The table reports two different temperatures, 25 and 50°C because heat favoured the color changing
 314 of the dyed samples. When the test was performed at RT (25°C) it was necessary to wait about 20 to
 315 30 min before noticing the color change. To speed up the process, after imbibitions of the samples
 316 into the buffered solutions, they were placed in oven for 10 min.

317 The reference sample to evaluate the ΔE of the fabrics was the polyamide 6.6 dyed at the conditions
 318 reported in paragraph 2.2.1. The data show that the dyed samples become darker by increasing pH,
 319 as L values decreased; moreover *a* and *b* tell us that the color of the fabrics changed from yellow to
 320 green (*a* evidences negative values) and blue (*b* had a sharp decrement). The color change was clearly
 321 visible by naked eyes.

322 3.4 Cotton gauze dyeing with Bromothymol blue

323 Bromothymol blue was selected to dye a cotton gauze as well. Before the dyeing process a dye fixing
 324 agent was used to improve the fastness of the dye. During multifibers textile dyeing cotton displayed
 325 a very poor dyeing yield. This may be attributed to the incomplete exhaustion and adsorption of the
 326 dye on the fibers, because the dyes can react not only with the fibre nucleophile but also with
 327 nucleophiles present in the dyebath, or because of dye hydrolysis [27]. The resin employed to fix the
 328 dye on cotton fibers was a polyamine based resin. In table 6 the fastness of the dye is reported.

329 **Table 6** Fastness of the dyed cotton gauze

	Washing fastness	Dry cleaning fastness	Light fastness
Bromothymol blue dyed cotton gauze	1/2	5	3/4

330

331 The results evidence a good dry-cleaning and light fastness. They represent good prerequisites for
 332 disposable applications.

333 Table 7 shows the results of the halochromic test performed with the Datacolor instrument. In figure
 334 7 the Cielab ΔE values are reported as a function of pH. The color difference was calculated according
 335 to eq. 1. The dyed cotton gauze was considered as the reference sample, pH was recorded as 4.5.

336

337 **Table 7** Colorimetric coordinates of the cotton gauze after immersion in different buffered solutions

338

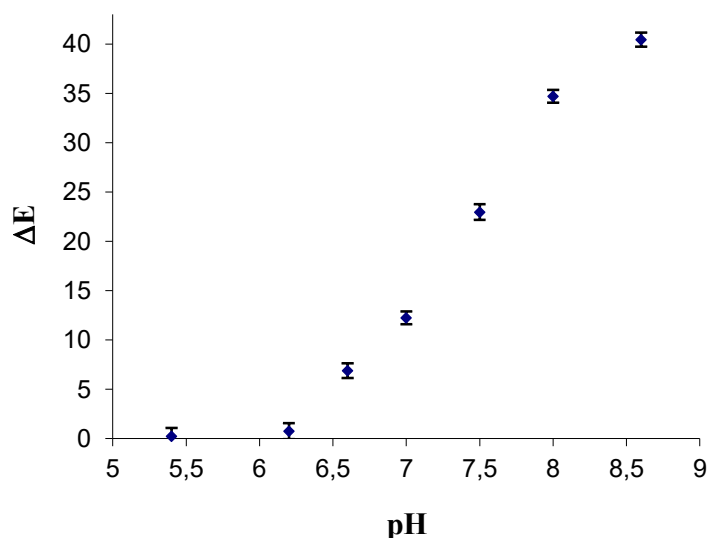
339

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341

342

pH	L	a	b	ΔE
5.4	72.83 \pm 0.53	13.76 \pm 0.82	57.54 \pm 0.91	0.25 \pm 0.84
6.2	71.10 \pm 0.49	10.36 \pm 0.59	54.01 \pm 0.22	0.76 \pm 0.81
6.6	70.54 \pm 0.86	10.30 \pm 0.52	53.62 \pm 0.66	6.90 \pm 0.75
7.0	69.40 \pm 0.41	8.75 \pm 0.96	51.71 \pm 0.58	12.24 \pm 0.65
7.5	63.54 \pm 0.67	4.14 \pm 0.62	44.19 \pm 0.90	22.97 \pm 0.80
8.0	61.01 \pm 0.81	-10.26 \pm 0.42	25.87 \pm 0.74	34.72 \pm 0.65
8.6	56.36 \pm 0.72	-15.07 \pm 0.53	12.51 \pm 0.66	40.45 \pm 0.71



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347

348

Fig. 7 ΔE values of the dyed cotton gauze against pH

349
350 The pH range was restricted from 5.4 to 8.6 in view of disposable medical applications. It is known
351 that in chronic wound skin pH turns from acidic to alkaline values and covers a pH range from pH
352 6.5 to 8.5 [28]. The dyed cotton gauze have shown halochromic properties in the pH interval of
353 interest. The dyed gauzes showed a visible color change. Particularly from pH 6.6 to pH 7.5 and 8.6
354 the color showed a shift from yellow to dark green. This was confirmed by the Datacolor analysis
355 that evidenced a decrease in L values as well as a decrease in a and b , meaning that the samples
356 became darker by increasing the pH. a and b values supported the visible color changes to a greener
357 extent. Figure 7 evidences broad ΔE values in the pH range from 6.6 to 8.6 that vary from 6.90 ± 0.75
358 to 40.45 ± 0.71 .

359 *3.5 Industrial dyeing with Bromothymol blue dye*

360 The industrial dyeing was carried out at Tintoria Finissaggio 2000 s.r.l. in an overflow filling machine.
361 An elastic cotton gauze and a linen textile fabric were dyed with Bromothymol blue
362 according to the conditions described in paragraph 2.2.2. After the dyeing process the textile
363 substrates were analysed in laboratory to test the dye fastness and the halochromic properties.

364 *3.5.1 Halochromic test*

365 The dyed samples were cut in rectangular specimens and dipped in the buffered solutions. The pH
366 range was set from pH 5.5 to pH 9.0. Table 8 reports the CIElab colorimetric coordinates as well as
367 the ΔE color differences.

368
369
370

371 **Table 8** Colorimetric CIElab coordinates of the dyed elastic cotton gauze and of the linen textile
 372 fabric, after immersion in the pH buffered solutions

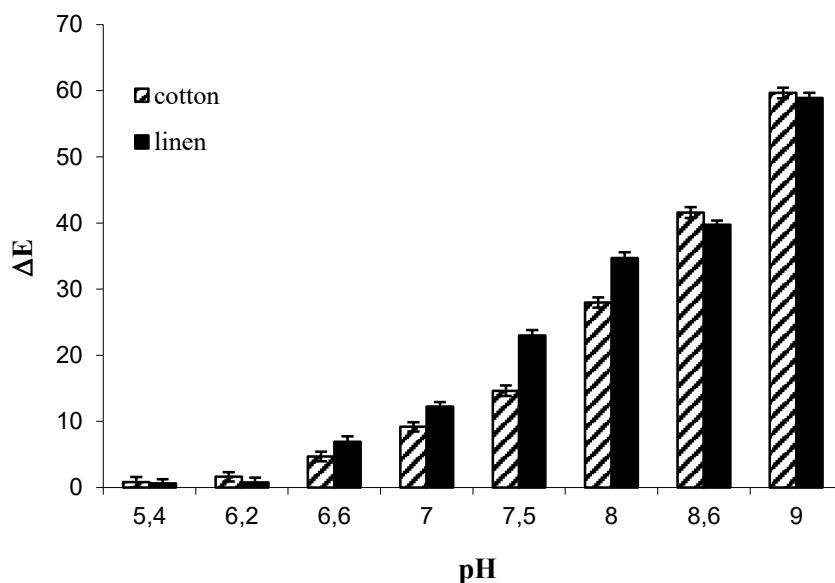
Cotton				
pH	L	a	b	ΔE
5.4	75.56±0.86	15.20±0.67	60.98±0.62	0.79±0.78
6.2	71.51±0.59	11.26±0.91	53.77±0.38	1.62±0.70
6.6	68.60±0.68	7.98±0.76	49.71±0.59	4.68±0.72
7.0	65.52±0.52	6.00±0.83	47.06±0.64	9.17±0.69
7.5	62.84±0.81	2.84±0.72	43.39±0.83	14.62±0.81
8.0	57.04±0.83	-3.91±0.65	33.28±0.67	27.98±0.78
8.6	58.83±0.83	-6.16±0.69	32.90±0.80	41.58±0.82
9.0	46.36±0.73	-17.34±0.75	6.14±0.76	59.66±0.81
Linen				
5.4	78.42±0.56	11.20±0.32	59.48±0.91	0.62±0.65
6.2	74.36±0.92	8.71±0.59	54.92±0.63	0.76±0.75
6.6	72.16±0.73	5.95±0.86	51.40±0.75	6.90±0.82
7.0	70.70±0.81	3.07±0.57	47.22±0.66	12.24±0.68
7.5	67.28±0.69	-0.47±0.69	42.50±0.92	22.97±0.83
8.0	62.42±0.82	-6.66±0.81	33.69±0.82	34.72±0.84
8.6	74.91±0.53	7.96±0.56	54.30±0.79	39.75±0.63
9.0	52.14±0.69	-17.44±0.84	12.02±0.67	58.91±0.79

373

374 The reference samples were the dyed elastic cotton gauze and the linen textile fabric as granted from
 375 Tintoria Finissaggio 2000 s.r.l. The data obtained evidenced a wide color change in the pH interval
 376 from 6.6 until 9.0, more appreciable in the graph of figure 8 that plots the ΔE values versus pH of the
 377 dyed samples. Table 8 shows a decrease in L values as well as in *a* and *b* by increasing the pH. For
 378 both linen and cotton the samples become darker and the decrement of *a* at negative numbers is the
 379 evidence that the samples turned into the CIElab field of green. The graph of figure 8 indicates that
 380 there is no appreciable difference in linen and cotton halochromic properties.

381

382



383
384 **Fig. 8** ΔE on the elastic cotton gauze and linen textile fabric against pH
385
386

387 *3.5.2 Dye fastness test*

388 Table 9 reports the results obtained after the evaluation of washing, dry-cleaning and light fastness
389 of the two textile materials industrially dyed.

390 **Table 9** Fastness of the industrial dyed textile materials

	Washing fastness	Dry cleaning fastness	Light fastness
Bromothymol blue dyed cotton gauze	1/2	5	3/4
Bromothymol blue dyed linen fabric	1/2	5	3/4

391

392 The results obtained demonstrated a poor washing fastness but a good dry-cleaning and light fastness,
393 which make the materials feasible for disposable applications.

394 **4. Conclusions**

395 Dyeing processes with halochromic dyes were performed on different textile materials. In the first
396 part of the work a multifiber textile fabric consisting of wool, polyacrylonitrile, polyester, polyamide
397 6.6, cotton and cellulose acetate strips, was selected to test the affinity of the dyes for the different
398 types of fibers. In the dyeing process no auxiliaries were added on purpose. The dyes employed have
399 shown affinity for wool and polyamide 6.6 fibers. A low affinity, not null however for cotton and

400 acetate was also highlighted. The halochromic test performed on the dyed samples evidenced the
401 maintenance of the halochromic properties of the dyes after adsorption on textile substrates. In
402 particular Curcumin manifested a color change in alkaline conditions; *m*-Cresol purple in the pH
403 range 4 to 7 on wool and cotton fibers; Chlorophenol red in a pH range from 7 to 10; bromothymol
404 blue in the pH interval from 4 to 10 for polyamide 6.6.; from 4 to 7 on wool and from 7 to 10 on the
405 other fibers. Washing and light fastness were evaluated; the dyes evidenced good washing fastness
406 on polyamide 6.6 and on wool. Light fastness was acceptable for Bromothymol blue and *m*-Cresol
407 purple.

408 In the second part of the work Bromothymol blue was selected to dye polyamide 6.6 and cotton.
409 Polyamide 6.6 showed a good dye adsorption as well as a good washing and light fastness. The
410 halochromic test performed on the dyed fabric evidenced a deep color change from acidic to alkaline
411 conditions. The fabrics turned from yellow to green. Temperature was necessary to speed up the color
412 change.

413 Cellulosic natural fibers manifested low affinity for the dye, so as a mordant step with a dye fixing
414 agent was necessary before the dyeing process. The halochromic test evidenced a clearly visible color
415 change from pH 6 to pH 9. The dyed samples evidenced good dry cleaning and light fastness.

416 The industrial trial carried out on cellulosic fibers confirmed the results obtained in laboratory so as
417 a scale up of the process might be feasible for disposable textile applications.

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420 Asse I Azione I.1b.1.2 Progetti collaborativi di ricerca e innovazione - Poli di Innovazione - Agenda
421 Strategica di Ricerca 2016 Linea A).

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