

# Fibers and Polymers

## Reversible and washing resistant textile-based optical pH sensors by dyeing fabrics with Curcuma

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# Reversible and washing resistant textile-based optical pH sensors by dyeing fabrics with Curcuma

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## Abstract

Curcuma powder was used to dye cotton and polyamide 6,6 fabrics in order to produce textile-based optical pH sensors. Both fabrics showed a bright yellow colour after dyeing and demonstrated colour changes (towards red) when contacted with basic solutions. Colour change and sensitivity differ for cotton and for polyamide. Curcuma-dyed cotton shows colour changes in particular in the range of pH between 6.5 and 8.5, whilst curcuma-dyed polyamide shows a wider pH range: from 8.5 to 13.0. The stability of pH sensing to washing was evaluated. Three different kinds of washing agents were used in order to simulate the real life conditions of a garment or a cloth. Standard test methods were used when available for washing tests. The pH sensing of the curcuma-dyed fabrics demonstrated an excellent fastness to all kinds of washing. Ionic strength of the solution does not affect the colour changes. Moreover, colour reversibility of the fabrics was proven, too. Colour change and reversibility of the fabrics was assessed by an UV-visible spectrophotometer. Spectral changes were observed at 540 nm for curcuma-dyed cotton, and at 487 and 574 nm for polyamide.

**Keywords:** Optical device, pH sensing, Textile sensor, Stability to washing, Colour reversibility.

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## 1. Introduction

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3 Optical sensors employ dyes that are able to change their optical properties on interaction with the  
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5 analyte of interest. Among optical sensors, pH sensing has received great attention because of the  
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7 importance of pH measurement in different fields ranging from healthcare to industrial applications  
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9 [1-3]. Currently, an emerging interest is in pH-sensitive dyes for textile application [4], which  
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11 would allow the fabrication of optical pH sensors with good sensitivity and stability. Significant  
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13 progress has been made on this subject [5-8]; however, inexpensive commercially available  
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15 products with high stability are still limited. On the other hand, the interest in the use of wearable  
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17 sensors to monitor health-related biometric parameters has been developed substantially in recent  
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19 years [9-13]. In particular, pH is an important parameter for several biological fluids or organs of  
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21 the human body. The pHs of skin, sweat, urine, wound liquids, etc. are supposed to be monitored by  
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23 using a textile-based pH sensors. Moreover, the pH is an important parameter also in industrial  
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25 applications such as liquid filtration, water depuration, food and beverage processing [14-18].  
26  
27 An appropriate optical pH sensor should include the real time response, reversibility, reproducibility,  
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29 and stability to real conditions. The pH range and the degree of dye leaching are also important  
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31 parameters. Optical sensors are attractive because they overtake some limitations of other types of  
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33 sensors (such as electrochemical sensors): they do not suffer from electrochemical and  
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35 electromagnetic interferences, they have low production cost and no energy consumption and they  
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37 offer the possibility of mass production [2].  
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39 Several natural colouring agents have been used as textile dyes, since they are believed to be safe  
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41 because of their non-toxic, non-allergic, and biodegradable nature. *Curcuma longa* L., collectively  
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43 known as turmeric, is used as colouring agent by food and textile industries (Natural Yellow 3,  
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45 Color Index 75300 - E100). The pigments in the extracts from rhizomes of *Curcuma longa* L.  
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47 (Zingiberaceae) are curcuminoids and its main component is curcumin [19]. Curcumin is a  
48  
49 hydrophobic polyphenol compound, which has a naturally yellow-orange colour. Curcumin  
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51 demonstrates keto-enol tautomerism: at basic medium the enolate form is prevailed form of  
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1 curcumin and in the pH range of 3-7, curcumin demonstrates the H-atom donor characteristic  
2 because of its keto form [20]. Recently, it has been reported that extracts from *Curcuma longa* have  
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4 pH sensitivity in solution showing different colour (from yellow to red) depending on the pH of the  
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6 extracting solutions [21-22]. Moreover, curcumin has been used as probe for the detection of  
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8 hypochlorous acid also in living cells with good selectivity [23].  
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10

11 Curcuma and curcuma-derived products have been applied to textile materials as dye [24-26] and  
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13 also as antifungal and antibacterial agents [27, 28]. Other properties of the use of curcuma as a pH-  
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15 sensitive dye for sensors in contact with human skin are related to its biological activities, such as  
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17 antioxidant, anti-inflammatory, and wound-healing [29]. Moreover, curcuma is a food-derived  
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19 product that should not produce health problems in case of leaching in applications for food  
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21 industry or water depuration. Finally, curcuma powder obtained by grounding and drying the  
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23 rhizomes is a cheap product.  
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28 In this work, commercially available curcuma powder derived from *Curcuma longa* was used to  
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30 dye cotton and polyamide 6,6 fabrics. The interaction between cotton or polyamide and curcuma  
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32 molecules involves weak intermolecular forces such as van der Waals and hydrogen bonding, due  
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34 to the enol structure of curcumin contained in curcuma [30, 31].  
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38 In the present work, we decided to evaluate colour changes of the curcuma-dyed fabrics at different  
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40 pH. Reversibility and stability of colour to washing and pH sensing were also evaluated.  
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43 This work also demonstrates that the substrate can affect the sensing of a dye. In fact, curcuma  
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45 shows a different range of pH in colour change and sensibility. In particular, curcuma-dyed cotton  
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47 shows colour changes in the range of pH between 6.5 and 8.5, whilst curcuma-dyed polyamide  
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49 shows a wider pH range: from 8.5 to 13.0.  
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52 In the second part of the work, we have considered that, from literature, curcumin contained in  
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54 curcuma can react with boron producing a red-brown compound [32-34]. Boron is an element  
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56 included in the buffer solutions used in the present work. Therefore, we conducted further pH  
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58 sensing and pH reversing tests through the immersion of the curcuma-dyed samples in different  
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1 basic pH solutions obtained with reagents without boron. Finally, ionic strength of each solution  
2 was considered.  
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4 Garments and, in general, clothing which have a direct contact with the skin are usually made of  
5 cotton, while, polyamide is used in technical applications such as Personal Protective Equipment  
6 (PPE) and filtration, including micro- and nano-filtration [14]. It is interesting to note that the pH  
7 range of colour change in cotton fabrics covers the pH values of the human skin. The pH values of  
8 the skin may depend on internal factors (e.g. hydration) or external factors such as detergent and  
9 cosmetics used in everyday life [35]. It is known that skin pH conducts an important role in the  
10 homeostatic maintenance of the skin barrier function and that normal skin pH is slightly acid at pH  
11 4.0-6.0. An increase in skin pH results in predisposition to mechanical trauma and reduces the  
12 integrity of stratum corneum [36], contributing to a dramatic skin barrier anomaly observed in skin  
13 diseases such as atopic dermatitis or in skin irritation and diseases [37]. A shift towards high pH  
14 values is called 'alkaline shift' and it is observed in chronic wounds, which most commonly have a  
15 pH range of 6.5-8.5 [38].  
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## 37 **2. Experimental**

### 38 *2.1 Materials*

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41 Fabrics were a plain cotton cloth with a weight of  $115 \text{ g m}^{-2}$  (according to ISO 105 F02:2009) and a  
42 plain polyamide 6.6 cloth with a weight of  $130 \text{ g m}^{-2}$  (according to ISO 105 F03:2001), supplied by  
43 Testfabrics Inc. (USA). Curcuma powder was supplied by Cannamela-Bonomelli srl (Italy).  
44  
45 ECE detergent (according to ISO 105-C06) by EMPA Testmaterials (Switzerland) and Tween® 20  
46 by Sigma-Aldrich (Germany) and tetrachloroethylene by Riedel-de Haën (Germany). Ethanol was  
47 supplied by Sigma-Aldrich (Germany).  
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58 In the first part of the work, solutions at different pH were: pH 4.0 solution was a buffer solution pH  
59 4.0, pH 6.5 was deionized water, pH 7.0 was a buffer solution pH 7.0, pH 10.0 was a buffer solution  
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1 pH 10.0, pH 7.5, 8.0, 8.5, 9.0 and 13.0 solutions were produced by dissolving sodium hydroxide (by  
2 Sigma-Aldrich) in deionised water. All the buffers listed above were purchased by Sigma-Aldrich  
3 (Germany). The pH values of each solution were measured by means of a Mettler Toledo  
4 FiveGo™ FG2 pHmeter, excepting for the commercial buffers (pH 4.0, 7.0 and 10.0).  
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9 In the second part of the work, pH 8.5, 9.0, 10.0, 11.0, 12.0, 12.8 solutions were obtained with  
10 different solutions of glycine (Sigma-Aldrich), sodium chloride (Sigma-Aldrich) and sodium  
11 hydroxide (Sigma-Aldrich).  
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## 17 2.2 Methods

18 A scheme of the whole procedure for producing and testing the samples is reported in Figure 1. It  
19 consists of the following steps: dyeing, washing, pH sensing and colour reversibility. Each step is  
20 described below. Figure 1 also reports the sample labelling.  
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30 *[Figure 1]*  
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### 36 2.2.1 Dyeing

37 Both fabrics were cut in rectangles with size 4 cm by 8 cm. Dyeing was different for cotton and  
38 polyamide. Cotton was treated with soda before dyeing in order to remove natural waxes of cotton  
39 fibres and to activate the fibre surfaces. The treatment was carried out using a solution of NaOH at  
40 the concentration of 2 % w/v in water, a liquor ratio of 80: 1 mL/g at 70 °C for 1 h under stirring.  
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43 To dye cotton, curcuma powder was dispersed in deionised water by stirring at the concentration of  
44 5% w/v for 20 h at room temperature. Cotton samples were soaked in the dispersion of curcuma for  
45 1 h under stirring at liquor ratio of 20:1 mL/g at room temperature. The wet samples were cured at  
46 120 °C for 5 h in an oven. Then the curcuma-dyed cotton samples were rinsed thoroughly in cold,  
47 running water for 10 minutes to remove the reagent exceedance and then dried completely at 50 °C  
48 for 2 h.  
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1 To dye polyamide, curcuma powder was dispersed in ethanol and deionised water (80:20 volume  
2 ratio) at the concentration of 5% w/v at 70 °C for 1 h under stirring. Ethanol was used in the dyeing  
3 bath because it was found to improve hydrophilicity of polyamide fabrics in other works [39, 40].  
4

5 Polyamide samples were soaked in the dispersion of curcuma for 1 h at 70 °C under stirring at  
6 liquor ratio of 80:1 mL/g. The samples were squeezed and dried at 50 °C for 2 h in an oven. Then  
7 the curcuma-dyed polyamide fabric samples were rinsed thoroughly in cold, running water for 10  
8 minutes to remove the reagent exceedance, and then dry again at 50 °C for 2 h.  
9

10 After dyeing, both cotton and polyamide samples showed a bright yellow colour. The samples were  
11 stored at least 24 h at controlled conditions (20 °C and 65 % relative humidity) before further  
12 testing.  
13

### 14 2.2.2 Washing

15 Samples from curcuma-dyed fabrics were washed once in a wash-wheel in different ways in order  
16 to investigate the effects of the three main classes of washing agents (i.e. anionic surfactants, non-  
17 ionic surfactants and solvents) on the sensing of the fabrics. The washing procedures were the  
18 following:  
19

- 20 a. 5 g/L standard soap (ECE) in water at 40 °C with a liquor ratio of 50:1 mL/g in order to  
21 simulate a domestic laundering, according to ISO 105-C01 (anionic laundering);
- 22 b. 1 g/L non-ionic detergent (Tween® 20) in water at 40 °C with a liquor ratio of 50:1 mL/g  
23 (non-ionic laundering);
- 24 c. pure tetrachloroethylene at 30 °C with a liquor ratio of 10:1 mL/g, according to ISO 105-  
25 X05 (dry cleaning).

26 Washing cycle lasted 30 minutes in all cases. For the procedures (a) and (b) after washing the  
27 samples were rinsed in cold water for 10 minutes, as requested by ISO 105-C01. Final drying was  
28 carried out at 50 °C for 2 h. For the procedure (c), the samples were gently squeezed, solvent  
29 evaporated in air in less than 1 h, then final drying was carried out at 50 °C for 2 h.  
30

1 After drying, the samples were stored at least 24 h at controlled conditions (20 °C and 65 % relative  
2 humidity) before further testing.  
3

### 4 5 6 7 *2.2.3 pH sensing*

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9 Washed and unwashed curcuma-dyed samples were contacted with solutions at different pH in  
10 order to evaluate the effectiveness of the fabrics as pH sensors. The pH values of the solutions were  
11 7.0, 7.5, 8.0, and 8.5 for cotton, and 8.0, 9.0, 10.0, and 13.0 for polyamide. The pH values were  
12 selected after preliminary tests that highlighted differences in the pH range of colour changing for  
13 curcuma-dyed cotton compared to curcuma-dyed polyamide. The different behaviours of the dyed  
14 substrates can be exploited in different fields, for instance in biomedical devices in contact with  
15 human skin for cotton, and in personal protective equipment or industrial applications (e.g.  
16 filtration) for polyamide.  
17

18 To test the sensing properties, the samples were soaked in 10 mL of solution at room temperature.  
19

20 After the immersion the colour immediately changed. The samples were pulled out from the  
21 solutions after 10 minutes, gently squeezed to remove the solutions as much as possible, and dried  
22 for over 24 h at controlled conditions (20 °C and 65 % relative humidity) on a filter paper. Then the  
23 samples were used for further testing.  
24

25 In the second part of the work, the same conditions were used to soak unwashed samples in pH 8.5,  
26 9.0, 10.0, 11.0, 12.0, 12.8 solutions. Since the pH range from 8.5 to 12.8 is the main range of  
27 sensitivity of polyamide samples, only polyamide samples were used to test the behaviour of  
28 curcuma in contact with basic pH solutions that do not contain boron.  
29

30 pH 8.5, 9.0, 10.0, 11.0, 12.0, 12.8 solutions were obtained by using the following Eq. 1:  
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$$32 \quad x \text{ ml of } a + (100 - x) \text{ ml of } b \quad (\text{Eq. 1})$$

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1 where  $a$  is glycine 0.1M in sodium chloride 0.1 M,  $b$  is sodium hydroxide 0.1 N, and  $x$  is the  
2 volume (in ml) namely, 94.7 for pH 8.5, 88.4 for pH 9, 62.5 for pH 10, 51.2 for pH 11, 46.0 for pH  
3  
4 12, 21.4 for pH 12.8. For each solution, the ionic strength has been calculated. Ionic strength of a  
5  
6 solution (I) is a function of the concentration of all ions present in the solution (Eq. 2):  
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$$10 \quad I = \frac{1}{2} \times \sum (c_i \times z_i^2) \quad (Eq. 2)$$

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17 where  $\frac{1}{2}$  is because both cations and anions are included,  $c_i$  is the molar concentration of ion  $i$  (in  
18  
19 mol/L),  $z_i$  is the charge number of the ion  $i$ .  
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21

22 In order to verify that the change of the colour of the samples is related only on the pH of the  
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24 solution and not on other parameters, such as the ionic strength, experiments were carried out at  
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26 different pH solutions with the same ionic strength of 0.15 M by adding proper amount of NaCl.  
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#### 31 *2.2.4 Colour reversibility*

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34 After the pH sensing tests, the samples were soaked for 10 minutes in 10 mL of deionised water  
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36 (pH 6.5) or buffer solution at pH 4.0 for cotton, and buffer solution at pH 4.0 for polyamide in order  
37  
38 to evaluate the reversibility of the colour change. The reversing was carried out at room temperature.  
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41 The samples were pulled out from the solutions, gently squeezed to remove the solutions as much  
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43 as possible, and dried for over 24 h at controlled conditions (20 °C and 65 % relative humidity) on a  
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45 filter paper. Then the samples were used for further testing.  
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#### 51 *2.2.5 Sample labelling*

52  
53 The scheme in Figure 1 reports the sample labelling. In brief, the samples after dyeing and washing  
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55 were labelled “CO+cur- $x$ ” for cotton and “PA+cur- $x$ ” for polyamide, where  $x$  can be “U” for  
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57 unwashed samples (i.e. samples just before dyeing), “A” for the samples washed with the anionic  
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1 standard detergent simulating domestic launderings, “B” for the samples washed with the non-ionic  
2 surfactant, and “C” for the samples after dry cleaning.  
3

4 The samples (washed and unwashed) after pH sensing were labelled as “CO+cur- $x$ - $y$ ” for cotton  
5 and “PA+cur- $x$ - $z$ ” for polyamide, where  $y$  and  $z$  are the pH values of the solutions used during the  
6 tests of the pH sensors. The pH values (i.e.  $y$  and  $z$ ) are 7.0, 7.5, 8.0, and 8.5 for cotton and 8.0, 9.0,  
7 10.0, and 13.0 for polyamide.  
8

9 Finally, in the label of the samples after colour reversibility were added the pH values of the  
10 solutions used to revert the fabric colour to the pristine one, pH 6.5 or 4.0 for cotton and pH 4.0 for  
11 polyamide, namely. Therefore the labels were “CO+cur- $x$ - $y$ →6.5” or “CO+cur- $x$ - $z$ →4.0” for cotton  
12 and “PA+cur- $x$ - $z$ →4.0” for polyamide.  
13

#### 14 2.2.6 Analysis

15 Scanning electron microscopy observations on the fabrics were carried out with a LEO (Leica  
16 Electron Optics) 435 VP scanning electron microscopy (SEM) at 15 kV acceleration voltage and 30  
17 mm working distance. Specimens were mounted on aluminium stubs and sputter-coated with gold  
18 before SEM observation in an Emitech K550 Sputter Coater with a current of 20 mA for 5 minutes  
19 in rarefied argon at 20 Pa.  
20

21 UV-visible spectra of the fabrics were acquired by means of a Perkin-Elmer Lambda 35 UV/VIS  
22 Spectrometer equipped with 50 mm diameter integrating sphere (RSA-PE-20). Spectra were  
23 recorded in a range between 400 and 700 nm with a data interval of 1 nm.  
24

### 25 3. Results and discussion

#### 26 3.1 Washing fastness of curcuma-dyed fabrics

27 In order to evaluate the stability of both colour and sensing properties to washing, samples of  
28 curcuma-dyed fabrics were subjected to three different washing procedures simulating the main  
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1 classes of these processes (domestic laundering, non-ionic laundering and dry cleaning). Anionic  
2 surfactants are widely used in house detergents for washing, as well as non-ionic are often added to  
3  
4 anionic surfactants in modern soaps for washing machines. In dry cleaning a liquid solvent is used  
5  
6 instead of water. The solvent depends on local legislation, but it is usually tetrachloroethylene.  
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9 Figure 2a shows a picture of curcuma-dyed cotton fabrics before and after washing. The samples  
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11 show a bright yellow colour after dyeing with curcuma. A slightly fading of the colour as a  
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13 consequence of anionic laundering is observed. The leaching of the dye from the fabric is confirmed  
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15 by the remaining water after washing with anionic laundering, which changed its colour from  
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17 transparent to light red. Dyed fabrics fade at a lower extent with non-ionic laundering, while dry  
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19 cleaning does not cause visible fading of the colour. On the opposite, the curcuma dye results very  
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21 resistant to each type of laundering in the case of polyamide fabrics (Figure 2b).  
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25  
26 By observing unwashed samples, we can note that curcuma-dyeing gives cotton and polyamide  
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28 fabrics different colours: while cotton assumes a bright yellow colour, polyamide assumes a darker  
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30 yellow colour. This is confirmed by the spectra reported in Figure 2c, which shows the absorbance  
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32 of undyed and dyed cotton and undyed and dyed polyamide fabrics in the range of visible  
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34 wavelengths. Curcuma-dyed cotton fabrics show a peak of absorbance around 465 nm, while  
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36 curcuma-dyed polyamide fabrics have a significant variation of absorbance values around 480 nm.  
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39 The peak of the polyamide fabric reaches higher value of absorbance, confirming the assumed  
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41 darker colour compared to the cotton fabric.  
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46 Figure 2d shows the effect of the washing on curcuma-dyed cotton fabrics. Anionic laundering  
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48 causes a decrease of the peak at 465 nm, according to the previous considerations: absorbance  
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50 decreases from 0.73 (unwashed) to 0.60 for non-ionic laundering and 0.54 for anionic laundering,  
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52 whilst the absorbance value on the samples after dry cleaning remains unchanged. Interestingly, in  
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54 the case of polyamide fabrics, the values of absorbance at the considered wavelength and the  
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56 spectral features do not change for all of the three kinds of laundering (Figure 2e).  
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[Figure 2]

### 3.2 pH sensing

Curcuma-dyed cotton fabrics show high sensitivity to little pH changes. As the pH increases, the yellow dyeing of both unwashed and washed samples becomes darkest, even if, for each tested pH, anionic- and non ionic-washed samples present a lighter colour compared to unwashed and dry cleaned samples (Figure 3).

Polyamide samples do not show any significant colour change up to pH 9, therefore the pH testing values were increased. Since tested pH values for polyamide fabrics are higher, polyamide fabrics result darker than cotton ones: from dark yellow for the samples contacted with the solution at pH 8 to brown for the samples contacted with the solution at pH 13 (Figure 4).

[Figure 3]

[Figure 4]

Moreover, on polyamide fabrics the effect of the washing on the resulting colour shade is less significant as compared to cotton.

Similarly, as regards pH sensing tests conducted in the second part of the work, with solutions of glycine, sodium chloride and sodium hydroxide, polyamide samples change their colour as consequence of the contact with basic medium and, again, the highest is the pH, the darkest is the colour assumed by the samples.

For each solution, ionic strength has been calculated. The results are reported in Table 1.

[Table 1]

1 In order to verify that the change of the colour of the samples is related only on the pH of the  
2 solution and not on other parameters, such as the ionic strength, we have repeated the experiment  
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4 preparing different pH solutions with the same ionic strength, that is 0.15. These solutions were  
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6 obtained using Eq. 1 and adding to each solution the needed amount of NaCl to reach a ionic  
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8 strength of 0.15.  
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11 pH sensing tests have been repeated by the immersion of curcuma-dyed polyamide samples in these  
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13 solutions. To the naked eye, the colours assumed by the samples after pH sensing test are the same  
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15 of the previous tests. As Figure 5 shows, ionic strength of the solution does not affect the colour  
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17 changes of the fabrics.  
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24 *[Figure 5]*  
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### 30 *3.3 Colour reversibility*

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32 The plots in Figure 3 show also the reversibility of the colour change on unwashed curcuma-dyed  
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34 cotton fabrics. Just contacting cotton samples with deionised water a nearly total reversibility of the  
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36 colour change to the original colour is observed. The reversibility becomes complete with the  
37  
38 contact with a pH 4.0 solution. This attitude is observed for each tested pH and it is remarkable also  
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40 in washed curcuma-dyed cotton samples.  
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44  
45 Figure 4 shows the pictures of unwashed curcuma-dyed polyamide samples contacted with pH 4.0  
46  
47 solution. Also in this case, the reversibility of the colour is total when samples are contacted with  
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49 pH 4.0 solution. This behaviour is observed in all polyamide samples, independently of the method  
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51 and of the reagents used to obtain different pH solutions.  
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54  
55 Pictures of polyamide samples contacted with deionised water have not been reported because it has  
56  
57 been noted that pH 6.5 of deionised water is not sufficient to observe the reversal of colour change  
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59 on these samples, neither of the three washings alters the properties of colour reversibility.  
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### 3.4 UV-visible spectroscopy

The contact with solution at different pH significantly changes spectral features of the samples, in agreement with the change in colour of the fabrics described above. In particular, a new absorption band is generated at about 540 nm for cotton and 574 nm for polyamide (both are visible as a shoulder of the main band); moreover, polyamide shows a great increase in the absorbance values at 487 nm.

UV-visible spectra of curcuma-dyed cotton samples shows the same trend for each spectra and, for both washed and unwashed samples, the highest is the pH, the highest are reached absorbance values as Figure 3 shows. Particularly significant is the trend at about 540 nm: at this wavelength, the effect of the pH on the value of absorbance becomes evident. For each sample, the contact with the solution at pH 7.0, 7.5, 8.0, 8.5 causes the increase of the absorbance value at 540 nm. Moreover, as expected, the contact with the highest pH (8.0 and 8.5) causes the greatest increase of the absorbance values. The contact with deionised water at pH 6.5 causes the return at lower values and the contact with the solution at pH 4.0 causes the total colour reversibility. It is interesting to note that this behaviour is reproducible and noteworthy on all the samples.

A similar behaviour is shown by UV-visible spectra of curcuma-dyed polyamide samples before and after the contact with solutions at pH 8.0, 9.0, 10.0 and 13.0, and reversibility after contact with a solution at pH 4.0 as Figure 4 shows. The contact with solution at high pH (e.g. 10.0 and 13.0) increases the absorbance of the peak at 487 nm and produces a shoulder centred at about 574 nm. Considerations about colour reversibility are analogue to the ones expressed for cotton samples, excepting for that curcuma-dyed polyamide after contact with solution at different pH does not reverse its colour by the simple immersion in water. The spectra of the samples before the contact with solutions at pH 8.0, 9.0, 10.0 or 13.0 are nearly indistinguishable from the graphs after the contact with solution at pH 4.0, to indicate the total reversibility of the colour change. By contacting

1 polyamide samples with solutions at higher pH, the reached absorbance values are higher than the  
2 ones reached by cotton samples.  
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4 For both cotton and polyamide, the contact with solution at pH 4 causes the complete return of the  
5 absorbance at the original value at the considered wavelengths for every type of samples (washed,  
6 unwashed and contacted with different pH).  
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10 For each of the considered wavelengths, the effect of the washing on the variation of the absorbance  
11 value has been evaluated, too. None of the three tested washings alters the behaviour of the colour  
12 response in terms of absorbance, which results the same of the unwashed samples. This means that  
13 the pH sensing property is not negatively influenced by the washing at all. For cotton samples, the  
14 responses related to anionic and non-ionic washing are slightly shifted downward, in agreement  
15 with the fading of the colour caused by these two launderings. For polyamide fabrics, only anionic  
16 washing produces a slight decrease in pH sensing.  
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28 UV-visible spectra of the samples contacted with different pH solutions obtained with glycine,  
29 sodium chloride and sodium hydroxide have the same trend of previous spectra: also in this case,  
30 spectra show a peak of absorbance at 487 nm and a shoulder at 540 nm.  
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36 Moreover, at the same pH, spectra have the same trend for the sample contacted with solution with  
37 ionic strength 0.15 and with solution with the initial ionic strength: polyamide samples show quite  
38 superimposable spectra at the same pH. These results confirm that the change of the colour does not  
39 depend on the ionic strength of the solution.  
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### 48 *3.5 SEM observation*

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50 SEM observation was carried out on each type of sample (i.e. pristine, dyed, washed, unwashed) of  
51 both cotton and polyamide in order to evaluate if curcuma dyeing and washing produce changes to  
52 the fibre surface. In Figure 6, pristine (a) and curcuma dyed (b) cotton samples are compared.  
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58 Particles having micro- and submicron dimensions are observed on the fibre surface in the dyed  
59 sample. Similar observation has been carried out on polyamide samples (Figure 7): while pristine  
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1 polyamide sample (a) shows fibres with a completely smooth surface, curcuma-dyed polyamide  
2 sample (b) and (c) shows particles with a morphology close to that observed in the cotton samples.  
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4 SEM observation was carried out also on polyamide sample after a treatment with ethanol and  
5  
6 deionised water (80:20 volume ratio), in order to be sure that this treatment does not produce any  
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8 effect on fibre surface: no particles have been observed on the fibres, therefore this excludes that the  
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10 treatment with ethanol and water produces changes to the fibre surface. SEM pictures have been not  
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12 reported here for the sake of brevity. Furthermore, this is in agreement with previous works [40, 41].  
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19 *[Figure 6]*  
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24 *[Figure 7]*  
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29 The presence of particles is more evident on polyamide samples than on cotton samples because of  
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31 the smoothness of the polyamide fibre surface. Therefore, further SEM investigation on the effect of  
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33 washing has been carried out on polyamide samples. Figure 8 shows SEM pictures of anionic-  
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35 washed (a), non ionic-washed (b) and dry-cleaned (c) polyamide samples. While dry-cleaned  
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37 polyamide sample shows a large amount of particles, anionic- and non ionic-washed samples  
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39 present a smooth and clean surface. This observation finds a correspondence with the exterior  
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41 aspect of these samples: while dry cleaning seems not to have a bleaching effect on the yellow  
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43 colour of the sample, anionic and non ionic-washed samples appear more faded and dim. However,  
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45 the removal of the particles due to the washing does not cancel the pH sensing of the fabrics since  
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51 the dyeing is not related to the particles alone.  
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56 *[Figure 8]*  
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#### 4. Conclusion

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2 Among optical sensors, pH sensing embedded on textile materials has received great attention  
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4 because of the importance of pH measurement in different fields ranging from healthcare to  
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6 industrial applications. Furthermore, the use of cheap and natural products for the production of  
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8 high technology devices is an emerging topic in sensing.  
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11 Curcuma was used as dye on cotton and polyamide 6,6 fabrics. Both fabrics (i.e. cotton and  
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13 polyamide) showed a bright yellow colour after dyeing and demonstrated colour changes when  
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15 contacted with basic solutions.  
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18 In particular, curcuma-dyed cotton seems to be more sensitive to colour change at pH between 7  
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20 and 8, and colour reversibility happens with satisfactory results to a higher pH (6.5) compared to  
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22 polyamide, which shows a wider pH range from 8.5 to 13.0 of colour change and reverts the colour  
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24 to the original only when contacted with a solution at pH 4.  
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28 Stability to washing of colour and pH sensing were evaluated. Three different kinds of washing  
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30 were used. Both colour and pH sensing of the curcuma-dyed fabrics demonstrated an excellent  
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32 fastness to washing. Moreover, colour reversibility of the fabrics was verified also on washed  
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34 fabrics. Colour change and reversibility of the fabrics were assessed by UV-visible spectrometry  
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36 measurements. Spectral changes were observed in particular at 540 nm for curcuma-dyed cotton,  
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38 and at 487 and 574 nm for polyamide.  
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42 Colour change seems not to be affected by the presence of boron, a particular element that can react  
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44 with curcumin, in the reagents used for pH sensing tests. Also, the ionic strength does not affect pH  
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46 sensing properties of curcuma-dyed fabrics.  
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## Tables

Table 1 - Ionic strength of different pH solutions.

pH of the solution	Ionic strength of the solution
8.5	0.1468
9	0.1445
10	0.1310
11	0.1265
12	0.1245
12.8	0.1090

## Figure captions

**Figure 1** - Scheme of the whole procedure for producing and testing the samples and summary of sample labelling.

**Figure 2** - Pictures of unwashed, anionic-washed, non-ionic washed and dry-cleaned curcuma-dyed cotton (a) and polyamide (b) samples. Spectra in the range of visible wavelengths of pristine cotton and polyamide compared with unwashed curcuma dyed cotton and polyamide samples (c). Spectra in the range of visible wavelengths of pristine cotton, unwashed, anionic-washed, non-ionic-washed and dry-cleaned curcuma-dyed cotton samples (d). Spectra in the range of visible wavelengths of pristine polyamide, unwashed, anionic-washed, non-ionic-washed and dry-cleaned curcuma-dyed polyamide samples (e).

**Figure 3** - Comparison between spectra of unwashed (a-d), anionic-washed (e-h), non-ionic-washed (i-l) and dry-cleaned (m-p) curcuma-dyed cotton samples before and after contact with solution at pH 7.0 (a), (e), (i), (m), at pH 7.5 (b), (f), (j), (n), at pH 8.0 (c), (g), (k), (o) or at pH 8.5 (d), (h), (l), (p), with water and with solution at pH 4. The reported pictures represent unwashed curcuma-dyed cotton samples after contact with solutions at pH 7.0, and 8.5.

**Figure 4** - Comparison between spectra of unwashed, anionic-washed, non-ionic-washed and dry-cleaned curcuma-dyed polyamide samples before and after contact with solution at pH 8.0 (a), (e), (i), (m), at pH 9.0 (b), (f), (j), (n), at pH 10.0 (c), (g), (k), (o), or at pH 13.0 (d), (h), (l), (p) and with solution at pH 4. The reported pictures represent unwashed curcuma-dyed polyamide samples after contact with solutions at pH 8.0, and 13.0.

**Figure 5** – Comparison between spectra of unwashed curcuma-dyed polyamide samples after contact with solutions with different ionic strength at pH 8.5 (a), 9 (b), 10 (c), 11 (d), 12 (e), 12.8 (f).

**Figure 6** - SEM pictures of pristine (a) and curcuma-dyed (b) cotton samples.

**Figure 7** - SEM pictures of pristine (a) and curcuma-dyed (b) polyamide samples. High magnitude picture of curcuma-dyed polyamide fibres (c).

**Figure 8** - SEM pictures of anionic-washed (a), non ionic-washed (b) and dry cleaned (c) curcuma dyed polyamide samples.

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# Figures

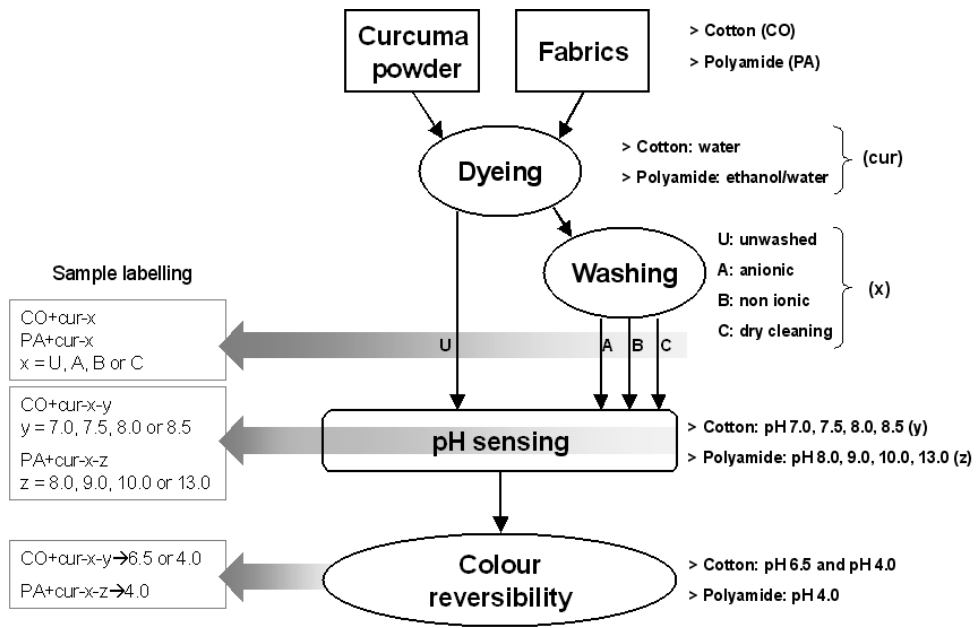


Figure 1

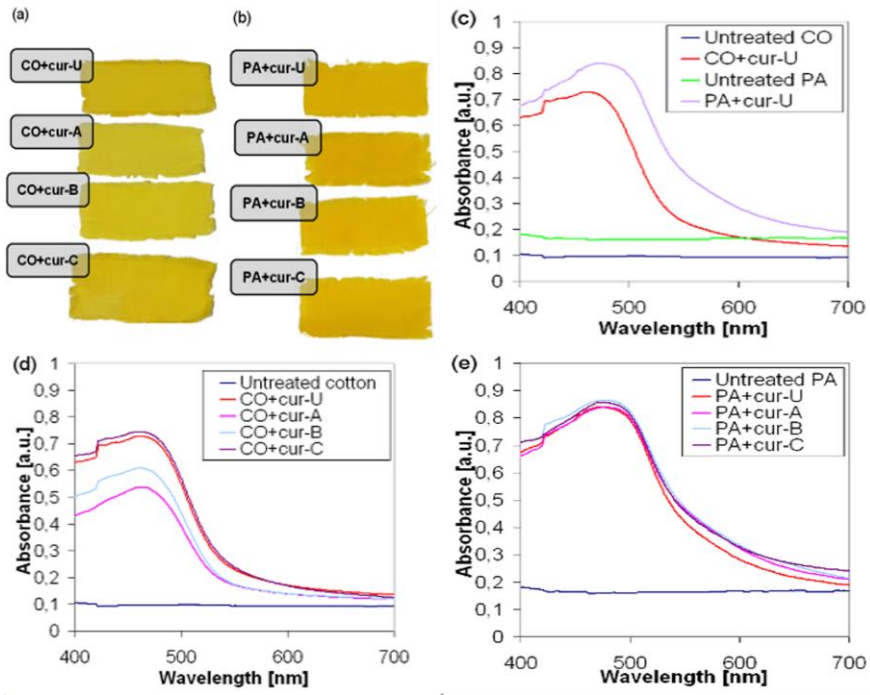


Figure 2

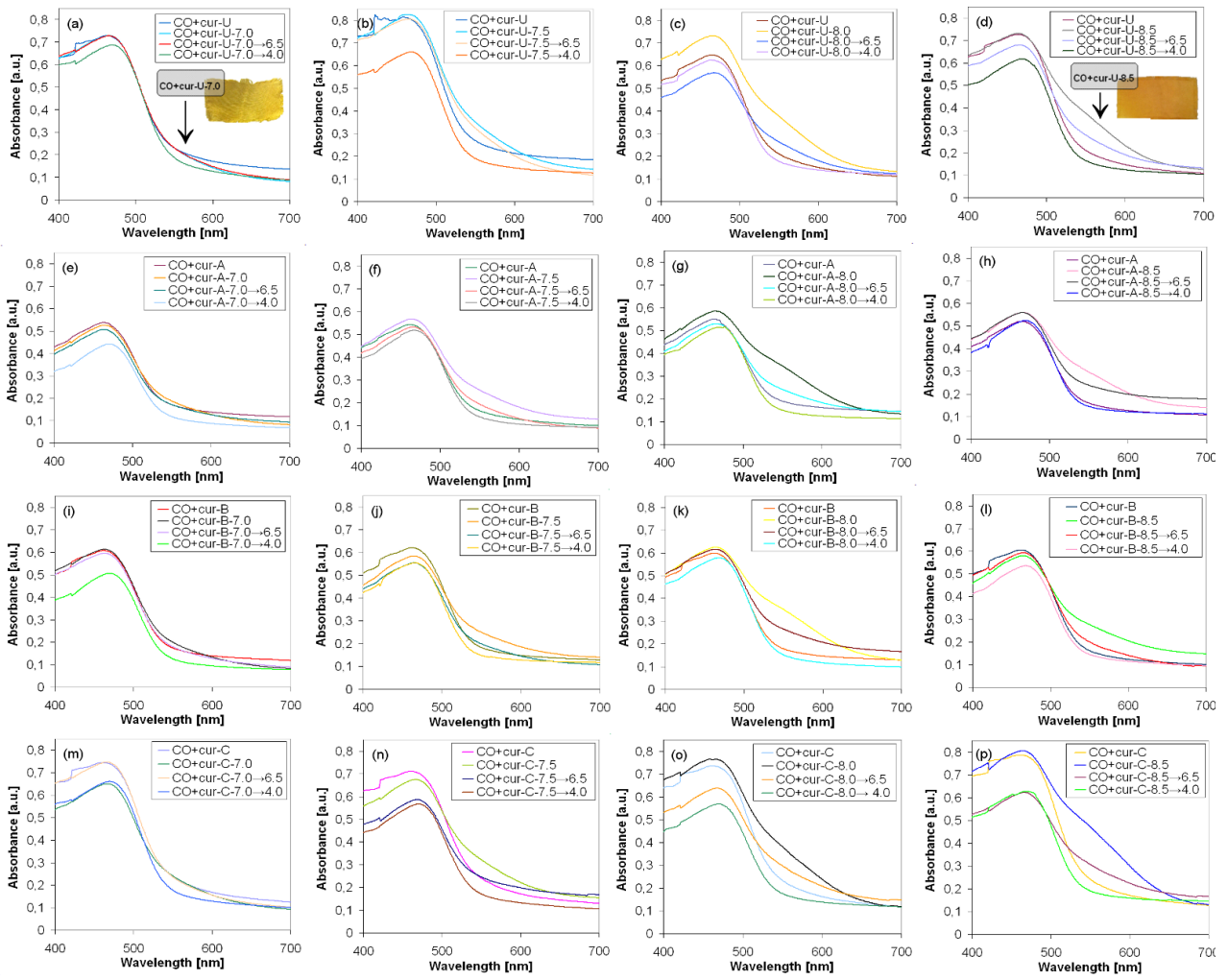


Figure 3

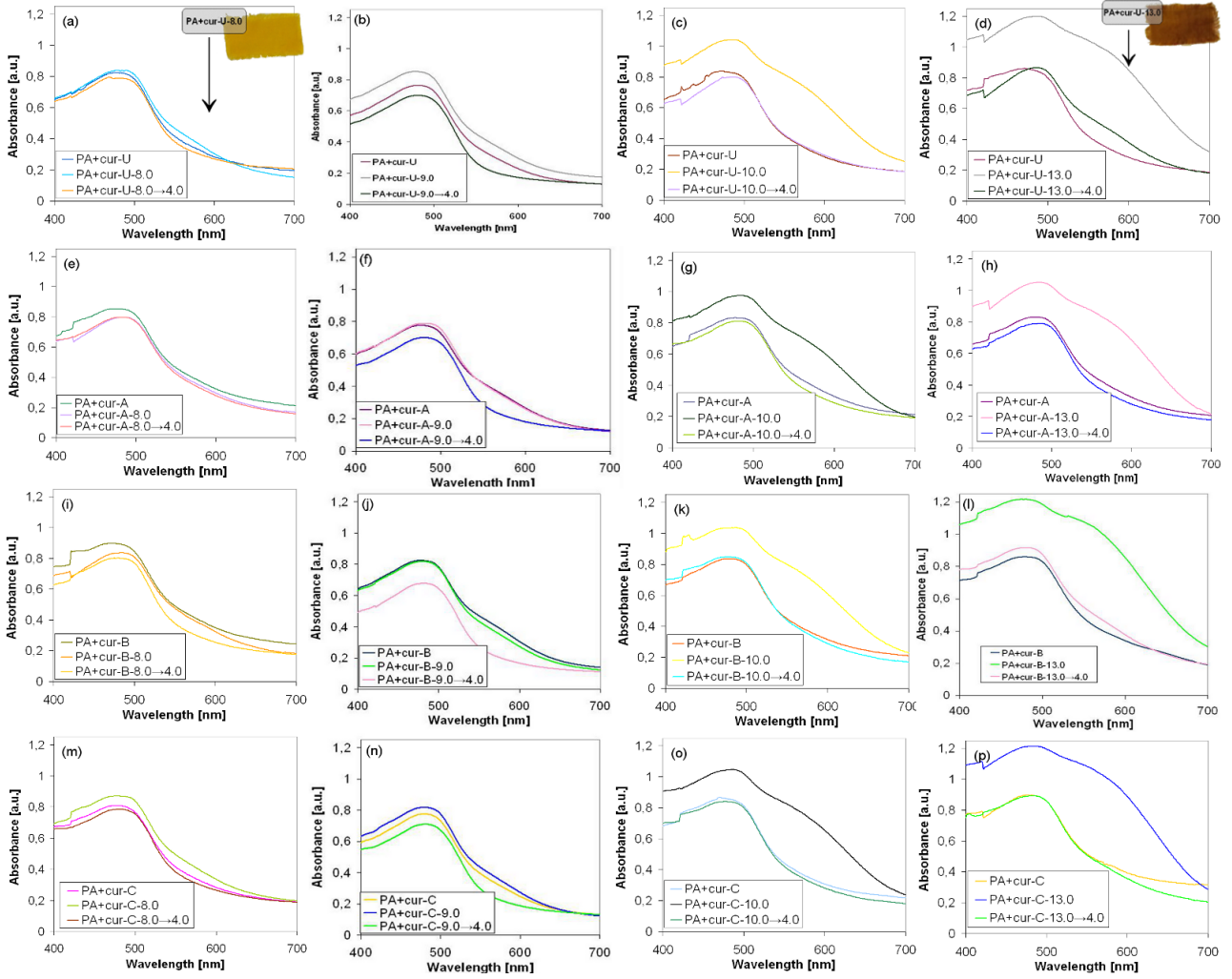


Figure 4

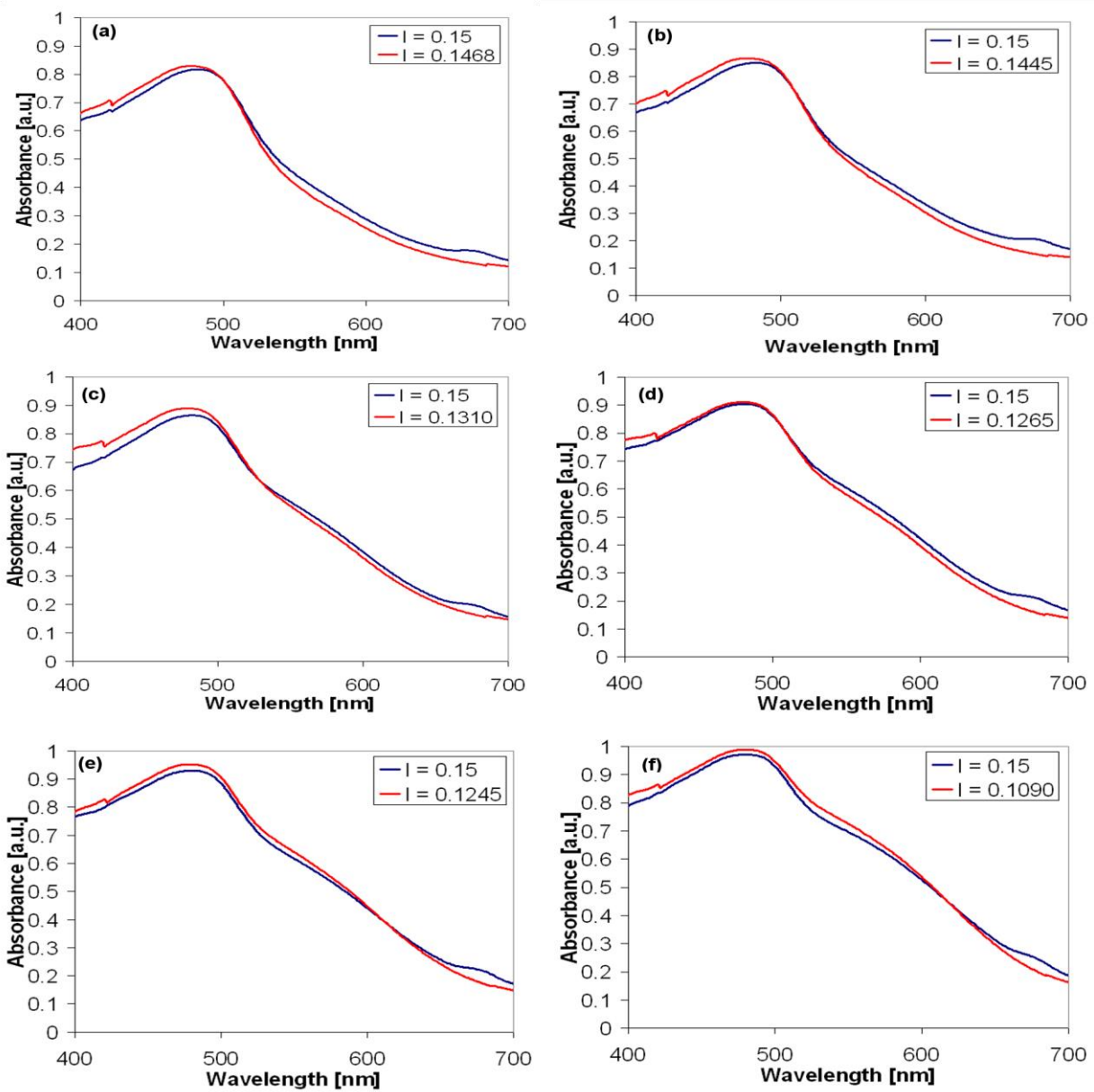
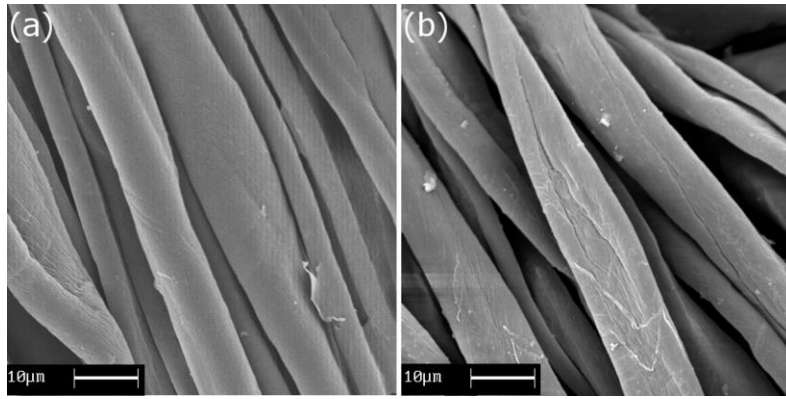


Figure 5



**Figure 6**

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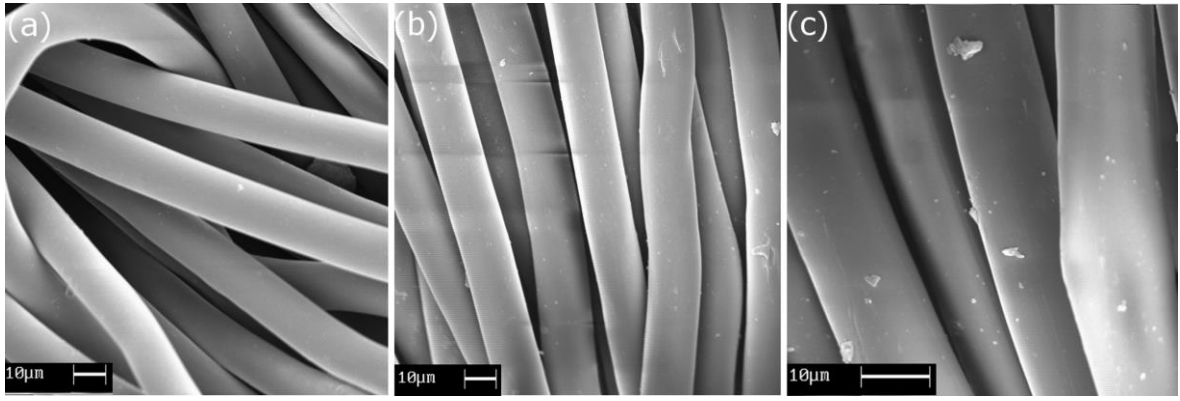


Figure 7

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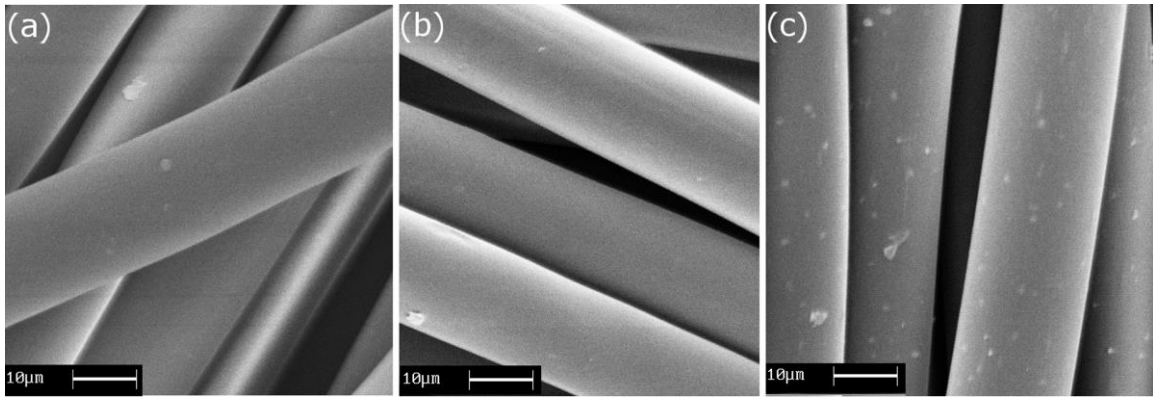


Figure 8

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