

Investigation of the pH-Sensing Properties of Anthocyanin-Dyed Silk Fabric Prepared Using Exhaustion Method

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Abstract

The study reports the successful fabrication of eco-friendly pH-sensing silk fabric utilizing silk woven fabric and anthocyanin dye extracted from Huyet du leaves (HD dye) via ultrasound-assisted extraction (UAE) with an aqueous ethanol solution. The dyeing process was conducted using an exhaustion method, maintaining a liquor-to-fabric ratio of 30:1 at temperatures of 60, 80, and 100 °C for durations of 30, 60, and 90 minutes. Comprehensive characterization of the dyed silk fabrics was performed using ultraviolet-visible (UV-Vis) spectra, CIE L*a*b* coordinates, color strength (K/S), color difference (ΔE), Fourier Transform Infrared Spectroscopy (FTIR), optical microscope, and pH-sensing capabilities. The results demonstrate effective incorporation of HD dye into silk fabric, with notable enhancements in color strength corresponding to increased dyeing time and temperature. Importantly, the pH-sensing properties of the dyed fabric displayed a “red-green traffic light” behavior in response to pH variations from 7 to 9, highlighting its potential for innovative smart textile applications.

Keywords: anthocyanin, Huyet du leaves, pH-sensing silk fabric, smart textile.

1. Introduction

Smart textiles have gained significant research interest due to their ability to interact with environmental stimulus [1, 9]. Among them, color-changing materials are particularly valued for their responsiveness to factors such as pH (halochromism), temperature (thermochromism), electric fields (electrochromism), light (photochromism), and solvent polarity (solvatochromism) [7, 10]. These dynamic properties enable real-time monitoring of environmental changes, making them highly relevant for protective clothing, environmental sensing, and biomedical applications [1, 2, 9].

Halochromic textiles, which change color in response to pH variations, hold particular promise [7, 10, 12]. However, research on their application using conventional dyeing techniques remains limited. Common approaches such as coating, extrusion, or microencapsulation often compromise durability and washability [10, 14]. Exhaustion dyeing, a widely used and sustainable method, offers better dye penetration and fiber-dye interaction, yet its effect on the halochromic properties of dyes requires further exploration [5, 13]. Potential interactions between dye

molecules and textile fibers may influence the protonation and deprotonation mechanisms responsible for color shifts, necessitating careful evaluation.

Halochromic textiles typically incorporate pH-sensitive dyes such as phthalides, triarylmethanes, fluoranes, and azo compounds [7, 8, 10, 15]. Recently, natural dyes, particularly anthocyanins, have gained attention for their non-toxic nature, abundance, and broad pH-dependent color spectrum [1, 5]. Anthocyanins are water-soluble flavonoid pigments responsible for the vivid red, blue, and purple hues commonly found in flowers, fruits, and leaves [3, 5, 15]. Chemically, they are glycosides, composed of sugar moieties attached to anthocyanidins - the aglycone forms of the pigments. While all anthocyanins share the same carbon skeleton, they differ in the nature and position of their substituent groups [3, 5]. The core structure is based on 2-phenyl chromenylium chloride (or flavylium chloride), with the most natural anthocyanins derived from 3,5,7-trihydroxy flavylium chloride. Various anthocyanins differ in the number and position of other hydroxyl groups, methoxy groups and sugar residue [3, 15, 16]. In addition to their well-documented antioxidant and anti-inflammatory activities,

anthocyanins display pronounced halochromic behavior, exhibiting reversible color changes in response to pH, making them suitable candidates for eco-friendly halochromic textiles.

Huyet du (*Cordyline fruticosa* L.) comprises over 480 species widely distributed throughout tropical and subtropical regions [3, 16]. In Vietnam, this ornamental plant is cultivated for its evergreen foliage, which ranges from glossy green to deep purples and variegated shades of red, yellow, and white [3, 5]. Its leaves are particularly rich in anthocyanin flavonoids, which can be effectively extracted using polar solvents such as water, ethanol, or methanol. Acidified extraction media are generally preferred, as low pH conditions enhance anthocyanin stability, facilitate cell membrane disruption, and reduce oxidation of phenolic compounds during the extraction process.

The anthocyanins derived from Huyet du leaves represent a sustainable and non-toxic alternative to synthetic dyes for textile applications [1, 4, 5]. When applied to silk, a protein-based biopolymer with high affinity for natural dyes, these pigments offer not only vibrant coloration but also functional responsiveness. Due to its biocompatibility, mechanical resilience, and excellent dye uptake, silk serves as an ideal substrate for the development of halochromic textiles.

This study examined the pH-sensing properties of silk fabric dyed with anthocyanins from Huyet du leaves via the exhaustion dyeing method. The dyed silk fabrics were analyzed for their halochromic performance using ultraviolet-visible (UV-Vis) spectroscopy, color strength (K/S), CIE Lab coordinates, Optical microscope and Fourier-transform infrared spectroscopy (FTIR). The influence of dyeing parameters such as

temperature and time on fabric dyeability was also investigated. The study aimed to develop a pH-sensitive textile sensor for practical applications, such as baby clothing care labels that visually indicate detergent residues.

2. Experiment

2.1. Materials

Huyet du leaves (HD leaves) were collected from a locality of the Hoai Duc district, Hanoi, Vietnam. First, the HD leaves were washed with distilled water, before being dried at 60 °C for 48 h. The dried leaves were thinly chopped into small pieces (5 mm × 5 mm) and kept in a sealable plastic bag for further study. Plain woven silk fabric (44 ends/cm, 32 picks/cm and weight per unit area of 56 g/m²) was purchased from Van Phuc traditional silk village, Hanoi, Vietnam. The silk fabric was washed at 40 °C for 60 min, rinsed with distilled water, and dried at 40 °C.

Analytical grade ethanol, formic acid, hydrochloric acid, potassium hydrogen phthalate, potassium chloride, potassium dihydrogen phosphate, potassium hydrogen phosphate, sodium hydroxide, and sodium bicarbonate were supplied by Xilong chemical industry incorporated Co. Ltd., China. All the experiments were carried out in triplicate and average values are reported.

2.2. Preparation of Huyet du Extract

The extraction process of HD dye was carried out following the procedure which had been published in our previous work [3]. In a typical procedure, Fig. 1, 4.0 g dried HD leaf samples were immersed in 20 mL aqueous ethanol solutions, kept in capped glass tubes, and then immersed in a water bath.

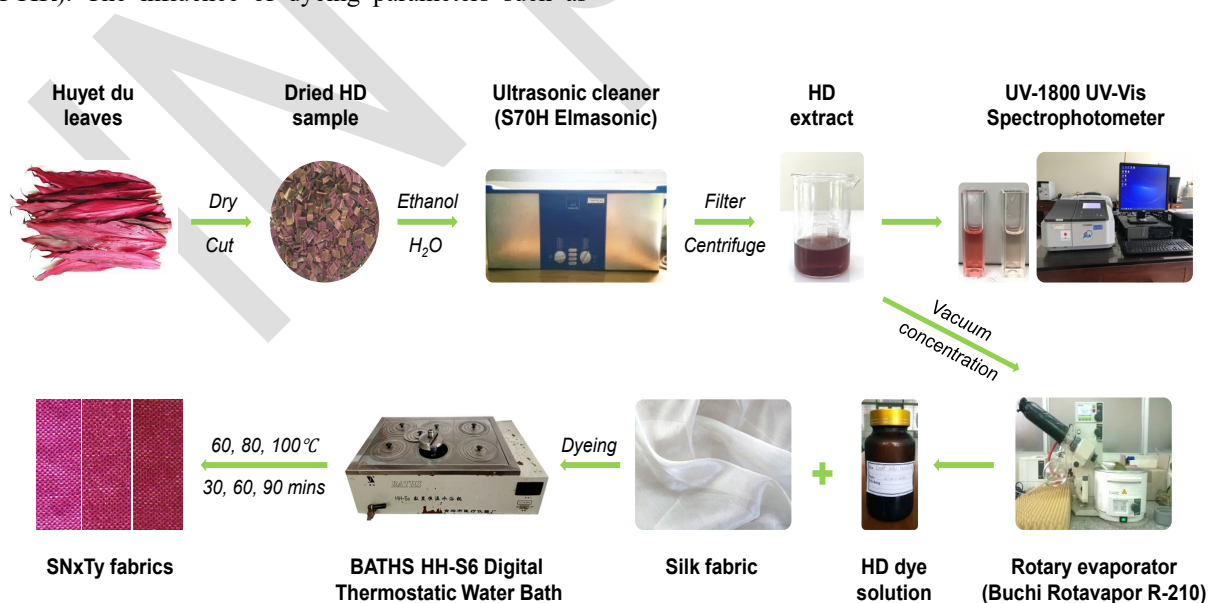


Fig. 1. Schematic diagram of UAE of natural colorant from Huyet du leaves and dyeing process of silk fabric with HD dye solution via exhaustion method

Ultrasound-assisted extraction (UAE) process was performed in Elma S70H Elmasonic (Germany) with the power and working frequency of 750 W and 37 kHz, respectively. The HD dye was extracted under optimal extraction conditions (70 °C, 94% ethanol concentration and 30 min sonication time), which were found out in our previous work [3]. After extraction, the tubes were immediately cooled to room temperature using chilled water. The extract solution was then filtered using a Whatman No.1 filter paper, then centrifuged at 10.000 rpm for 20 min. The obtained HD supernatant was analyzed using the pH differential method to determine the total anthocyanin content (TAC) of the HD extract [3].

2.3. Preparation of pH-Sensing Silk Fabric

The silk fabrics were dyed with HD dye in a digital thermostatic water bath (BATHS HH-S6, China) using an exhaustion method. The dyeing process was performed using HD dye solutions containing anthocyanin (TAC of 70 g/l) with concentration of 2 mL/l with different temperatures (60, 80, and 100 °C) for durations of 30, 60, and 90 minutes, in a 1:30 ratio bath. The dyeing line diagram of silk fabrics with HD dye was presented in Fig. 2. After dyeing, the dyed samples were rinsed with cold water then air-dried.

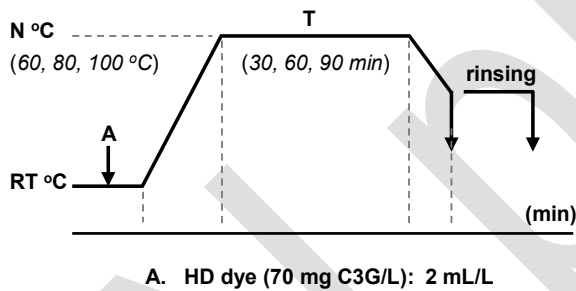


Fig. 2. Exhaust dyeing line diagrams of silk fabrics with HD dye

2.4. Characterization of pH-Sensing Silk Fabric

a. Color analysis

To evaluate dyeing performance, the color strength (K/S) and CIELAB of the dyed silk samples were determined using a reflectance spectrophotometer (X-rite, Ci4200) with D65 illumination, 10° observer. The K/S was calculated by the Kubelka–Munk equation (1).

$$K/S = (1 - R)^2/2R \quad (1)$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the fractional reflectance.

The color difference was expressed as ΔE^* and was calculated by the following equation (2):

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (2)$$

where ΔE^* is the CIELAB color difference between batch and standard. ΔL^* denotes the difference between lightness (where $L^* = 100$) and darkness (where $L^* = 0$), Δa^* is the difference between green ($-a^*$) and red ($+a^*$) and Δb^* is the difference between yellow ($+b^*$) and blue ($-b^*$).

b. Morphological analysis

The morphologies of the undyed and dyed silk fabrics with HD dye were characterized via a light microscope (DM500, Leica, China) coupled with a digital color camera (CMOS 16Mpx, Mesdan, China).

c. Fourier transform infrared spectrophotometry analysis

Fourier transform infrared spectrophotometry (FTIR) (Thermo Nicolet 6700 FTIR spectrometer, USA) were used to confirm the HD dye was presented into silk fabric.

d. The pH sensing test

The sensitivity of the HD dyed silk to pH variations was evaluated by dipping samples (1 cm × 1 cm) in buffer solutions from pH of 1.0 to 13.0. The methodology involved the preparation of a total of 7 buffers, as detailed in Table 1. Each sample was individually tested by fully submerging it in the corresponding buffer for 3 minutes at ambient temperature. In most cases, visible color changes were observed and recorded within 30 seconds of immersion.

Table 1. Buffering system choice for the colour assessment of pH-sensing silk fabric

pH value	Concentration (mol/L)	Buffering system
1	0.1	Potassium chloride/ Hydrochloric acid
3	0.1	Potassium hydrogen phthalate/ Hydrochloric acid
5	0.1	Potassium hydrogen phthalate/ Sodium hydroxide
7	0.1	Potassium dihydrogen phosphate/ Potassium hydrogen phosphate
9	0.1	Sodium bicarbonate/ Sodium hydroxide
11	0.1	Sodium bicarbonate/ Sodium hydroxide
13	0.1	Sodium bicarbonate/ Sodium hydroxide

3. Results and Discussion

3.1. Preparation of pH-Sensing Silk Fabric

The Huyet du leaf is known to contain several bioactive compounds, including anthocyanins, saponins, flavonoids, flavonols, chlorophylls, and glycosides, with anthocyanins being one of the predominant constituents of its extract [3, 5]. The primary molecular structure of anthocyanin identified in this study is cyanidin-3-

glucoside (C3G), illustrated in Fig. 3a. Analysis of the ultraviolet-visible (UV-Vis) spectra of the Huyet du extract at pH 1.0 and pH 4.5 (Fig. 3b) revealed a total anthocyanin concentration (TAC) of 70 mg C3G/L. In this research, the anthocyanins extracted from Huyet du leaves were utilized as a pH indicator for dyeing silk fabric, thereby facilitating the development of pH-sensing textiles.

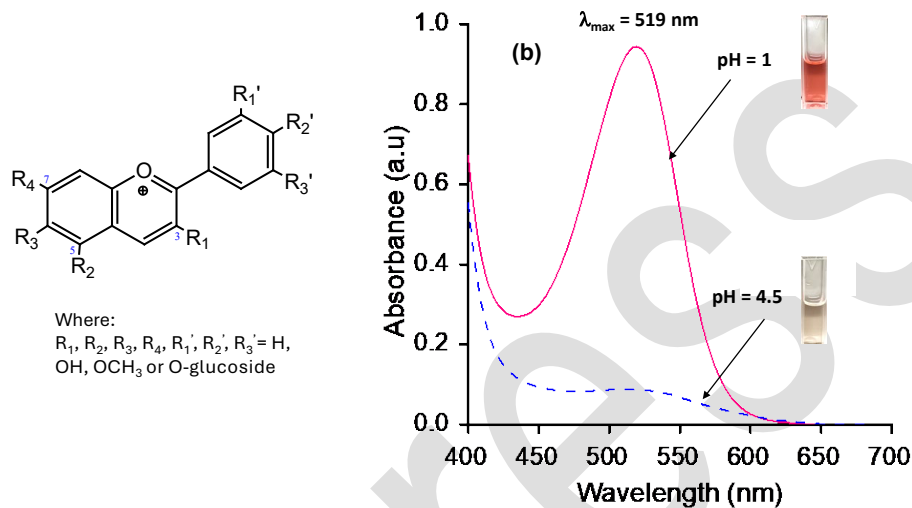


Fig. 3. (a) The molecular structure of anthocyanin, and (b) UV-Vis spectrum of HD extract

Table 2. L*, a*, b*, C*, H*, and K/S values of the dyed silk fabric samples

Sample	L*	a*	b*	C*	H*	K/S	Scan sample
SN1T1	58.41	18.71	-2.51	18.88	352.36	1.62	
SN1T2	55.75	19.48	-1.11	19.51	356.73	1.95	
SN1T3	55.85	18.09	-0.17	18.09	359.47	1.89	
SN2T1	55.05	19.48	0.44	19.49	1.30	2.05	
SN2T2	43.62	20.70	3.74	21.04	10.25	4.32	
SN2T3	43.30	20.17	6.78	21.28	18.59	4.37	
SN3T1	53.66	22.55	-3.55	22.83	351.07	2.37	
SN3T2	42.78	23.42	1.18	23.45	2.89	4.85	
SN3T3	32.03	21.56	3.70	21.78	9.75	5.36	

To investigate the dyeability of silk fabrics using HD dye, the dyeing process was conducted at various temperatures (N1 = 60, N2 = 80, and N3 = 100 °C) and for different durations (T1 = 30, T2 = 60, and T3 = 90 minutes). In order to evaluate the HD dye pickup into the silk fabrics, the colorimetric data (L^* , a^* , b^* , C^* and H^*), color differences (ΔE^*) and color strength (K/S) of the dyed fabric samples were determined. The results presented in Table 2 indicate that increasing both the dyeing temperature and duration significantly enhanced the color strength (K/S values) of the dyed silk fabric samples (denoted as SNxTy, where x is from 1 to 3 and

y is from 1 to 3). Specifically, at a dyeing temperature of 60 °C (N1), the color difference (ΔE^*) increased to 3.1 and 3.5 when the dyeing time was extended to 60 and 90 minutes, respectively, compared to the SN1T1 sample dyed for 30 minutes. At a higher temperature of 100 °C, the corresponding ΔE^* values rose markedly to 11.9 and 22.8 for the 60- minute and 90-minute dyeing durations, respectively, relative to SN3T1. These results indicate that temperature plays a more dominant role than time in influencing dye uptake, as elevated temperatures enhance dye diffusion and facilitate deeper penetration of the dye molecules into the silk fabric.

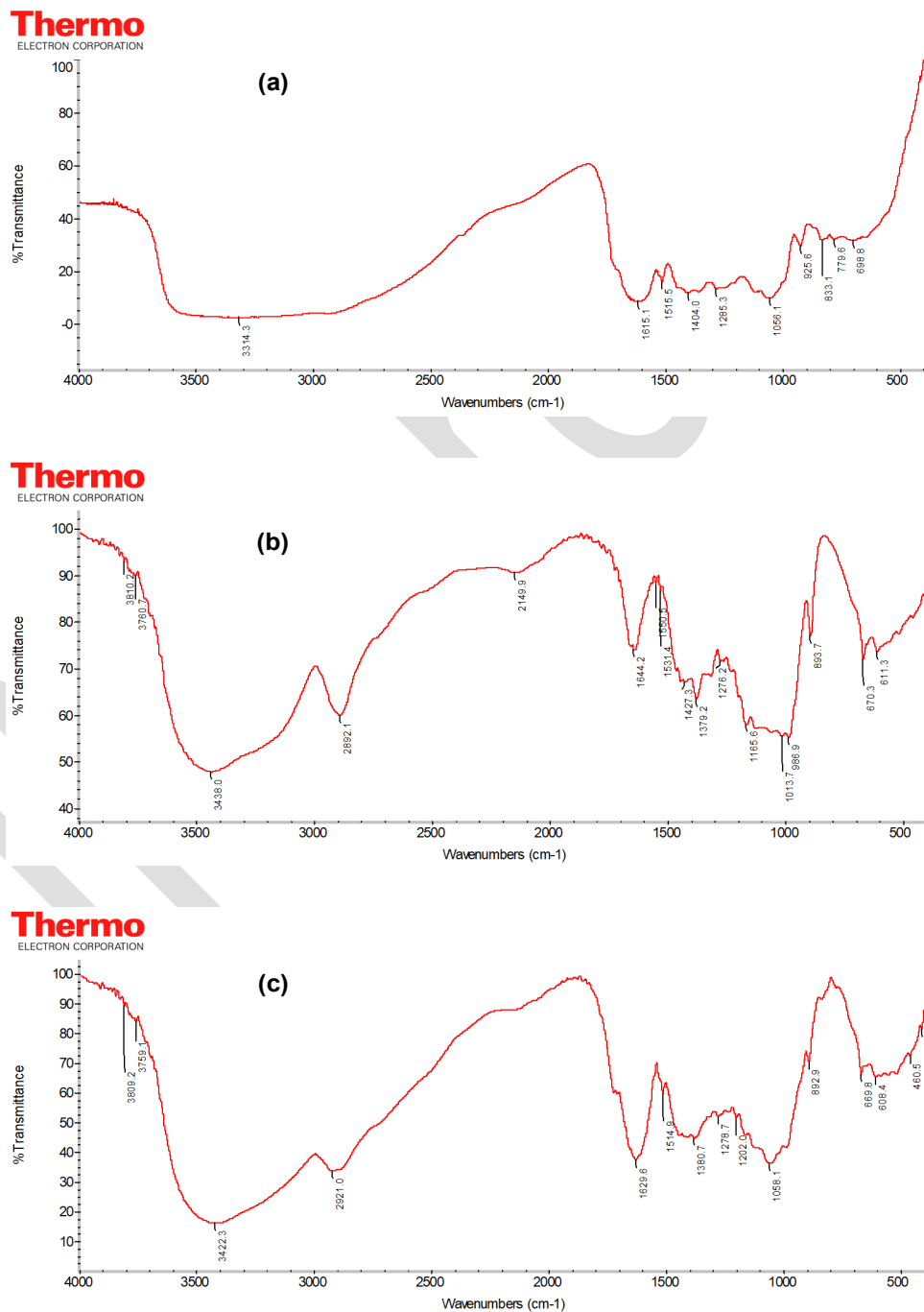


Fig. 4. FTIR spectra of (a) the HD dye, (b) original silk fabric, and (c) the dyed silk fabric

In addition, the anthocyanin-based dye extracted from Huyet du demonstrated high thermal stability under all tested dyeing conditions. This is further supported by the observed increase in K/S values, which reflected more intense coloration at elevated temperatures and longer dyeing durations. The improved dye-fiber interaction can be attributed to the formation of hydrogen bonds between the hydroxyl groups of anthocyanins and the amine and hydroxyl functional groups present in the silk's polypeptide macromolecules. Such interactions likely enhance dye fixation, contributing to both the color intensity and fastness of the dyed silk fabrics.

Fig. 4a displayed the FTIR spectrum of the HD dye extracted in aqueous ethanol solvent. The hydroxyl (-OH) group is observed at a peak of 3314 cm^{-1} , while the C-C bonds in the cyclic structure appeared at peaks of 1615 cm^{-1} and 1285 cm^{-1} . The secondary amine group was identified at a peak of 1515 cm^{-1} , and the C-O group in esters was noted at 1056 cm^{-1} [3]. These findings confirmed the presence of various anthocyanin compounds in the dye extracted from Huyet du leaves.

The FTIR spectrum of the original silk fabric (Fig. 4b) revealed a significant number of peaks,

indicating the presence of multiple compounds with diverse functional groups in the silk fibroin. Characteristic peaks included 3438 cm^{-1} (-OH), 2892.1 cm^{-1} (C-H), 1644.2 cm^{-1} (primary amine) and 1531.4 cm^{-1} (secondary amine) [7].

The FTIR spectrum of the silk fabric dyed with HD dye at $80\text{ }^{\circ}\text{C}$ for 60 minutes (SN2T2, Fig. 4c) showed that most peaks correspond to those of original silk fibroin, with a notable peak at 1515 cm^{-1} that aligns with the FTIR spectrum of HD dye. This peak was absent in the spectrum of the undyed silk fabric, providing strong evidence that the anthocyanin dye had successfully bonded to the silk fabric.

Fig. 5 presented optical microscopic images of silk fabric before and after dyeing with HD dye at $80\text{ }^{\circ}\text{C}$ and 60 minutes. The pristine silk fabric exhibits a plain-woven structure and a bright surface (Fig. 5a). The original silk fabric consists of yarns composed of a bulk of fibroin filaments, with an average yarn size of $70\text{ }\mu\text{m} \pm 9\text{ }\mu\text{m}$. In contrast, the dyed silk sample displayed a darker coloration, confirming that the HD dye had effectively linked to the silk fabrics.

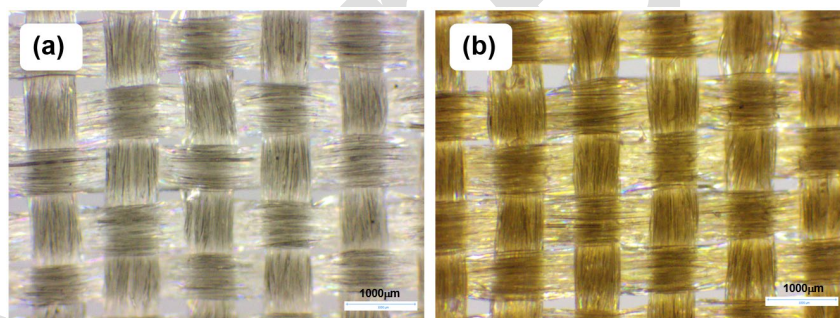


Fig. 5. Optical microscope images of (a) pristine silk fabric and (b) dyed silk fabric

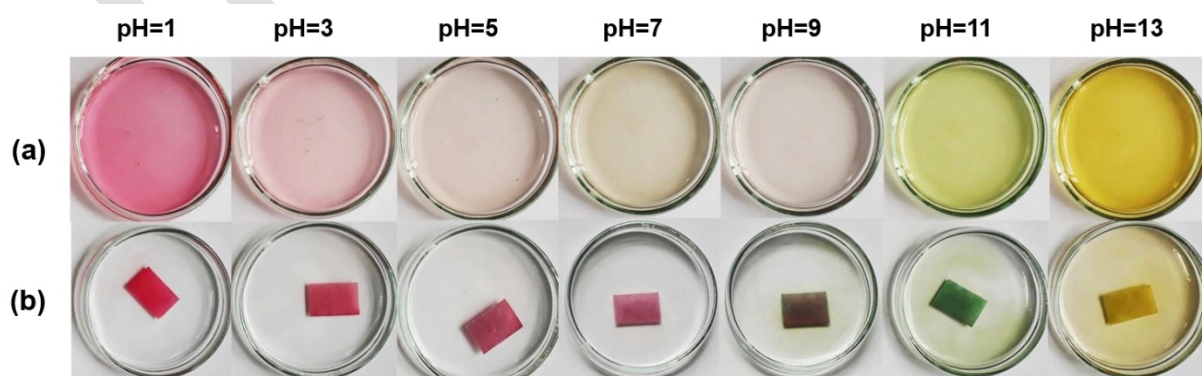


Fig. 6. (a) The color of HD dye solution upon pH changes. (b) The dyed silk fabrics after dipping in different buffer solutions

3.2. Interaction of HD Dye and the Dyed Silk Fabrics with Different pH Solutions

Fig. 6 illustrated the color changes of the HD dye aqueous solution across a pH range from 1 to 13. The solutions transitioned from red to green and finally to yellow as the pH increased, a phenomenon attributed to the protonation and deprotonation of anthocyanin molecules in the HD dye in response to varying acidity and alkalinity [1, 3, 7]. In detail, the HD dye solution appeared red at a strongly acidic pH of 1. As the pH increased, the color gradually shifted from red to dark pink, then to green, and finally to yellow at pH of 13. At pH levels of 7 and 9, the quinoidal base underwent further deprotonation, resulting in the formation of resonance-stabilized quinone anions (anionic quinoidal base), which led to green in color.

The color changes observed in the HD-dyed silk fabrics were consistent with those of the anthocyanins in the HD dye solutions as the pH varied from 1 to 13 (Fig. 6). Interestingly, the dyed fabric exhibited a "red-green traffic light" behavior in response to pH variations between 7 and 9, aligning with the changes observed in the HD dye solutions. These findings suggested potential applications for the design of naturally dyed fabrics, such as food freshness monitoring or care labels for baby clothing, enabling visual detection of detergent residues post-washing through colorimetric changes in response to pH variations during the drying process.

4. Conclusion

Among optical sensors, pH sensing embedded on textile materials has attracted significant attention due to the critical role of pH monitoring across diverse fields, including healthcare and industrial applications. Moreover, the integration of low-cost, natural materials into advanced sensing technologies represents a growing area of interest in sustainable sensor development. This research presents a simple exhaustion dyeing method to produce halochromic textiles taking advantage of the flexibility, biocompatibility, and lightness of silk, along with the unique halochromic properties of the HD dye, which transitions from red to blue as the pH increases from 7 to 9. The study investigated the color strength, morphological structure, dye-fabric interactions, and pH-sensing capabilities of the pH-responsive silk fabric. The results confirm that silk fabrics functionalized with the HD dye hold significant potential for various applications in smart textile materials, including biomedical, sports, and protective clothing.

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