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A green route to covalently fluorescent whitening cotton fabric for excellent washing durability and skin safety via electron beam irradiation

Kai-Xuan Huo[1] · Yong-Chang Song[1] · Yu Meng[1] · Zi-Qiang Wang[2] · Ming Yu[1] · Bo-Wu Zhang[1] · Jing-Ye Li[1]

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Abstract

Herein, a new method was developed for efficient and lasting fluorescent whitening cotton fabric by synthesizing and using a vinyl-containing fluorescent whitening agent to covalently grafting onto fiber surfaces with the assistance of electron beam irradiation. The results from FT-IR spectroscopic, X-ray photoelectron spectroscopic, and energy dispersive spectrometric analyses showed that the fluorescent whitening agent was successfully anchored on cotton fiber via radiation-induced grafting copolymerization. The optimized whiteness value at 110.81 (that of raw cotton fabric, 74.50) was achieved using just 0.3 wt% fluorescent whitening agent. Notably, the whiteness value of the treated cotton fabric remained 110+ even after 100 equivalent home-washing cycles, substantiating its excellent washing durability. Skin stimulation experiments on rabbits showed that the primary stimulation index of all experimental groups was 0 and no abnormal clinical symptoms were found in all tested rabbits, demonstrating the outstanding skin safety. Furthermore, energy generated by irradiation grafting technology was much lower than that of traditional processes and water consumption greatly reduced. Even the effluent from this process completely met the discharge standard of industrial wastewater without any treatment. This study explores a new method for textile finishing via electron beam irradiation, providing a green and sustainable perspective for the textile industry.

Keywords Fluorescent whitening · Cotton fabric · Electron beam irradiation · Washing durability · Skin safety · Sustainable

1 Introduction

With the increasing demand for functionalization and esthetics of textiles [1, 2], fluorescent whitening agents have been widely used in textile finishing processes [3]. Owing to the noncovalent binding with textiles [4, 5], fluorescent whitening agents always have low utilization in finishing processes (only 60–70%) [6] and are prone to wash-out in household laundry [5, 6]. The effluents from textile finishing and washing also contain difficult-to-treat fluorescent whitening agents [7, 8], which are harmful to the aquatic ecological environment and subsequently to human health [9, 10]. Also, the wash-out of fluorescent whitening agents from fabrics results in textile color deepening, reducing its marketing value. Therefore, efforts are necessary to improve the finishing utilization and washing durability of fluorescent whitening agents on fabric.

As a powerful tool, high-energy radiation technology has been used frequently in the field of textile and fiber modification [11–16]. Electron beam is used to treat textile

Kai-Xuan Huo and Yong-Chang Song have contributed equally to this work.

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✉ Bo-Wu Zhang
zhangbowu@shnu.edu.cn

✉ Jing-Ye Li
jyli@shnu.edu.cn

[1] MOE Key Lab of Resource Chemistry, Joint International Research Laboratory of Resource Chemistry of Ministry of Education, Shanghai Key Laboratory of Rare Earth Functional Materials, and Shanghai Frontiers Science Centre of Biomimetic Catalysis, Shanghai Normal University, Shanghai 200234, China

[2] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

wastewater which is difficult to degrade [17]. A large number of novel functional fabric and fiber materials with superhydrophobicity [18, 19], heavy metal ions and dyes [20], adsorption [21], antibacterial [22], antistatic [23, 24], and photothermal properties [25, 26] have been developed with the assistance of electron beam or gamma-ray irradiation. Recently, our group has found that both disperse and reactive dyes with vinyl groups can be covalently grafted onto fiber surfaces under high-energy radiation, which not only improved dye utilization but also enhanced color fastness [27–31]. As it well known, covalent bonds (3–4 eV of bond energy) of the chains in fibers are easily broken by high-energy radiation (1–5 MeV), thus generating free radicals on fibers, which rapidly initiate the graft polymerization of vinyl monomers. The covalent bonds between fibers and graft segments contribute to a permanent functionalization [32]. This is why a novel dyeing method based on high-energy radiation achieves high dye utilization and excellent color fastness. The chemical oxygen demand (COD) of wastewater from this process is so low that it meets direct discharge standards [28, 31]. Besides that, this radiation-induced dyeing method significantly reduced the use of various finishing reagents in textile functional modification and has the characteristics of low energy consumption, easy operation, and fast processing speed [33, 34]. Undoubtedly, this is an efficient and environmentally friendly textile processing method, which could promote the traditional textile industry's transformation in the direction of green and sustainable development.

Inspired from this, a new vinyl-containing fluorescent whitening agent, (E)-6,6'-(ethene-1,2-diyl) bis (3-((4,6-bis(2-(acryloyloxy) ethoxy)-1,3,5-triazin-2-yl) amino) benzenesulfonic acid), was synthesized using 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSDA), cyanuric chloride (CC), and hydroxyethyl methacrylate (HEA) as starting reagents. For brevity, the new fluorescent whitening agent was named as DCH. The DCH was further used to whiten raw cotton fabric with the assistance of electron beam irradiation. The route is summarized in Fig. 1. FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and energy dispersive spectrometry (EDS) were used to confirm the success in fluorescent whitening of cotton fabric under electron beam irradiation. Standard accelerated washing (AATCC61-2006) and light fastness tests (ISO 105-B02: 2014) were conducted to evaluate the wash-durable and sunlight-durable fluorescent whitening effect. Skin safety of the whitened cotton fabric was tested on adult female New Zealand white rabbits according to the international testing standard (ISO 10993-23: 2021). Furthermore, the wastewater from this electron beam irradiation-induced fluorescent whitening process was tested by a COD meter and electrical conductivity meter to assess the content of spent organic matters and salts. This study provided a new method

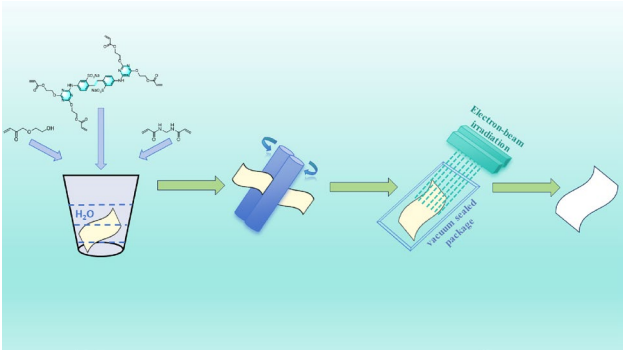

Fig. 1 (Color online) Fluorescent whitening process of raw cotton fabric under electron beam irradiation

to textile finishing process with low pollution and energy consumption, superior to the traditional chemical finishing methods, contributing to the transformation, and upgrading of the textile industry.

2 Experimental

2.1 Synthesis of DCH

The synthetic route included two steps (Fig. 2). The first step was synthesis of an intermediate, ((6-chloro-1,3,5-triazine-2,4-diyl) bis (oxy)) bis (ethane-2,1-diyl) diacrylate. The details were as follows: Hydroxyethyl methacrylate (HEA, 300 mL), cyanuric chloride (CC, 50 g, 0.271 mol) and 4-hydroxy-2,2,6,6-tetramethyl-piperidinooxy(4 H-TEMPO, 15 g) were added to the reaction flask. N,N-diisopropylethylamine (DIPEA, 50 mL, 0.287 mol) was slowly added dropwise in an ice water bath. After this addition, the reaction was stirred for 30 min and DIPEA (50 mL, 0.287 mol) then added. The oil bath was heated to 30 °C for 2 h, and the reaction monitored by thin layer chromatography (TLC). The organic phase was washed with water until the HEA was washed out, then dried with anhydrous sodium sulfate and ethyl acetate removed in vacuum to obtain the intermediate. Yield: 84%. ESI-MS (CH_3OH) m/z: calculated for $[M+H]^+$,($C_{13}H_{14}ClN_3O_6^+$) 343.0570, found 344.0621. ^{1}H-NMR (400 MHz, DMSO-d6) δ 6.35 (dd, J = 17.2, 1.6 Hz, 1 H), 6.20 (dd, J = 17.3, 10.3 Hz, 1 H), 5.97 (dd, J = 10.3, 1.6 Hz, 1 H), 4.69–4.52 (m, 2H), and 4.48 – 4.35 (m, 2H). ^{13}C-NMR (101 MHz, DMSO) δ 171.93, 171.85, 165.78, 132.64, 128.36, 67.22, 62.38, 40.58, 40.42, 40.37, 40.22, 40.17, 40.01, 39.96, 39.75, 39.54, and 39.33.

The second step was the reaction between the above intermediate and 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSDA). In the reaction flask, DSDA (0.74 g,0.002 mol), anhydrous sodium carbonate (0.212 g,0.002 mol), water

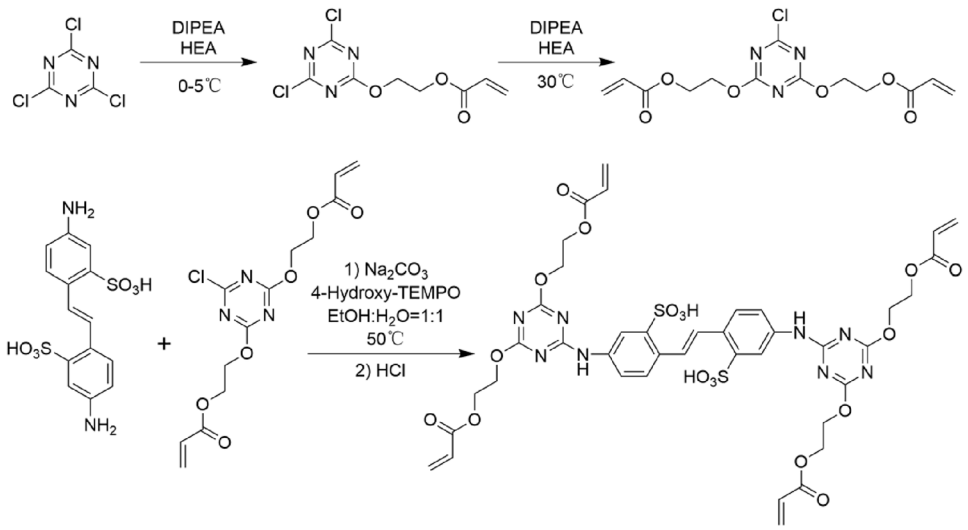

Fig. 2 Synthetic route of DCH

(10 mL), and 4 H-TEMPO (0.086 g) were added and stirred to dissolution. The above intermediate (1.72 g, 0.005 mol) was uniformly dispersed in ethanol (10 mL). After stirring the suspension, it was poured into the reaction flask and heated in the oil bath at 50 °C for 2 h. During the reaction, saturated sodium carbonate solution was added dropwise to control the pH at 7. After the reaction, the HCl solution (0.2 M) was slowly added dropwise until a yellowish solid was precipitated. The solid was filtered, washed with anhydrous ethanol, and vacuum dried to obtain a yellowish solid powder (DCH). Yield: 80.2%. ESI-MS (CH_3OH) m/z: calculated for $[M-H]^-$ ($C_{40}H_{40}N_8O_{18}S_2^-$) 984.19, found 984.1794. ^{1}H-NMR (400 MHz, DMSO-d6) δ 10.32 (s, 1H), 7.72 (dd, J = 8.6, 2.4 Hz, 1H), 6.36 (dd, J = 17.3, 1.7 Hz, 1 H), 6.22 (dd, J = 17.3, 10.3 Hz, 1H), 5.97 (dd, J = 10.2, 1.7 Hz, 1H), and 4.74−4.40 (m, 4H).^{13}C-NMR (101 MHz, DMSO) δ 166.06, 165.88, 146.00, 137.31, 132.56, 130.44, 128.49, 126.62, 126.11, 121.12, 119.63, 66.05, 62.85, 40.50, 40.29, 40.09, 39.88, 39.67, 39.46, and 39.25.

2.2 Fluorescent whitening of raw cotton fabric by electron beam irradiation

Raw cotton fabric with a size of 25 cm × 15 cm was thoroughly washed with plenty of deionized water and then dried in a drying oven. DCH solutions with certain concentrations were prepared by rigorously stirring at room temperature, with HEA and N,N'-methylenebisacrylamide (MBA) added as assistant ingredients. The dried cotton fabric was fully immersed in the above solution. A cotton fabric ginning machine (Fig. S1) with a pressure of 1 bar and a speed of 2 m min^{-1} used to press the raw cotton fabric. The DCH solution was squeezed into the gaps of the raw cotton fabric to remove excess solution, such that the DCH was evenly distributed on the raw cotton fabric. The treated cotton fabric sample was vacuum sealed in a plastic bag and irradiated by a self-shielding electron accelerator (1.5 MeV, Shanghai Institute of Applied Physics, CAS, Shanghai, China) for 10 kGy of absorbed dose at room temperature. After irradiation, the treated cotton fabric was taken out and washed in deionized water (60 times to the sample mass) under 90 °C for 3 min. Finally, the washed cotton fabric was dried in a vacuum oven at 60 °C. The spent washing water was collected and tested using COD and electrical conductivity meters. A series

Table 1 Method for fluorescent whitening of cotton fabric by electron beam irradiation

Sample	Mass of DCH (g)	Mass of Na_2CO_3 (g)	Mass of HEA (g)	Mass of MBA (g)	Mass of H_2O (g)	Concentration
FWC-1	0.03	0.0032	0.03	0.02	30	0.1%
FWC-2	0.09	0.0097	0.09	0.06	30	0.3%
FWC-3	0.15	0.0162	0.15	0.10	30	0.5%
FWC-4	0.24	0.0259	0.24	0.16	30	0.8%
FWC-5	0.3	0.0323	0.3	0.20	30	1%

of whitened samples were prepared by adjusting the concentration of fluorescent whitening solution (Table 1) and named as FWC fabric, respectively.

The utilization rate can be calculated by Eq. (1)

$$\text{Utilization Rate}\ (\%) = \left(1 - \frac{n_w A_w}{n_0 A_0}\right) \times 100\% \quad (1)$$

where n_w and A_w are the dilution ratios and absorbance of the washing wastewater and n_0 and A_0 the dilution ratios and absorbance of the whitening solution after irradiation at doses of 10 kGy in nitrogen, respectively.

2.3 Whiteness measurements

The fluorescent whitening sample was measured using a Datacolor 800 spectrophotometer (Technical Color Solutions, USA), and untreated cotton fabric was used as the raw cotton fabric. A D65 light source was selected as the test light source. Each sample was measured three times on any surface of the fabric and the average whiteness recorded.

2.4 Washing and light fastness test

The fluorescent whitening sample was cut to a size of 50 mm × 150 mm. To evaluate the washing fastness of the whitening cotton fabric, according to the AATCC61-2006 test method, the accelerated washing durability test was carried out using condition 2A and one of the accelerated washing cycles equal to five home washing cycles. The washed cotton fabric was washed with distilled water at 40 °C and dried at 60 °C. The fluorescent whitening sample was measured using the Datacolor 800 spectrophotometer and the change curve of whiteness with washing time drawn.

The fluorescent whitening sample and a set of reference samples (grade 4 blue wool standard samples) were exposed under an artificial light source according to the prescribed conditions and then the sample and reference samples compared for color changes to evaluate color fastness. This test is based on ISO 105-B02: 2014 Method 3. As fluorescent whitening textiles usually use 3–4 level blue wool standard sample test level, the 4 level blue wool standard sample test level was used in this test.

2.5 Skin safety test

Three healthy adult female (not pregnant, not produced) New Zealand white rabbits were selected for skin safety testing. The samples are fluorescent whitening cotton fabric and blank gauze. Within 24 h before administration, hair removal was performed on both sides of an animal's back. The hair removal area should meet the application needs, and the hair removal area was about 10 cm × 15 cm

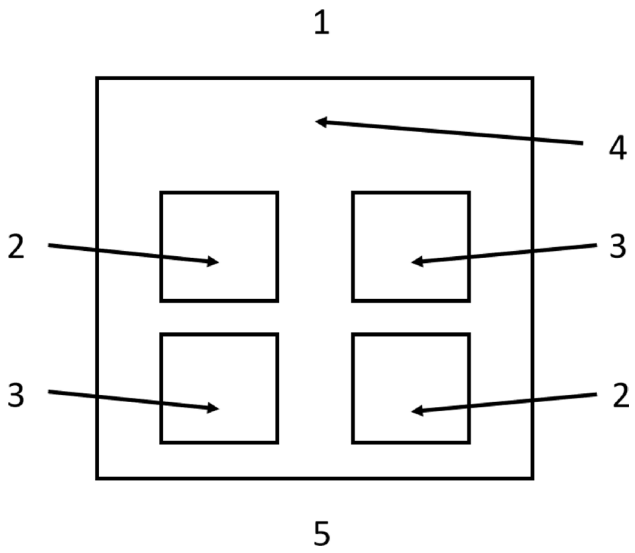

Fig. 3 Location of skin application sites: Cranial end (1), test site (2), negative control site (3), clipped dorsal region (4) and caudal end (5)

(Fig. 3). The sample was cut into small pieces with an area of 2.5 cm × 2.5 cm, and the sample directly attached to the corresponding depilated skin, and then a layer of cellophane and four layers of gauze applied. Finally, medical tape was used for sealing and bandaging. After 4 h of application, the sample was removed and the administration site marked with an oily marker pen. The residual sample on the skin was washed with warm water and dried. Blank gauze was used on the control site. The operation of administration was the same as that of the sample. The erythema and edema reactions of animal skin were observed at 1 ± 0.1 h, 24 ±2 h, 48 ±2 h, and 72 ± 2 h after removing the patch. The score was evaluated according to the observation results and the primary irritation index (PII) calculated according to Eq. (2), expressed as

$$PII = \frac{\sum_1^{n_1} A}{n_1} - \frac{\sum_1^{n_2} N}{n_2}, \quad (2)$$

where n_1 is the times of scores in the administration area, A is the total score of the administration area, n_2 is the times of scores in the negative control area, and N is the total score of the negative control area.

3 Results and discussion

3.1 Structural analysis of DCH

The chemical shifts of the hydrogen atoms contained in vinyl ranged from 5.8 to 6.6 in ^{1}H-NMR, which were clearly seen (Fig. 4a). The high proportion of vinyl groups in DCH

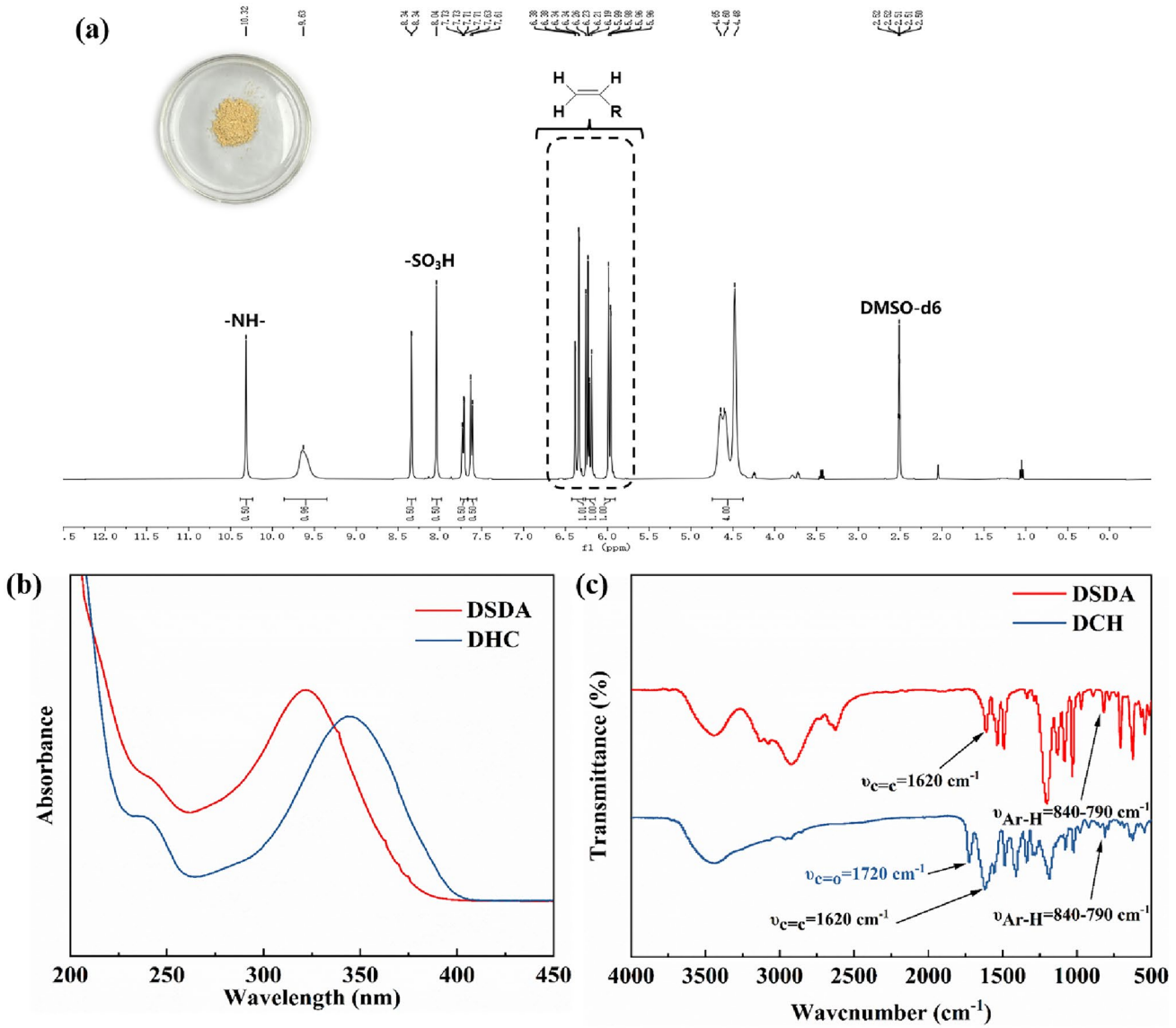

Fig. 4 (Color online) ^{1}H-NMR of DCH (**a**), UV absorbance spectra of DSDA and DCH (**b**), and FT-IR spectra of DSDA and DCH (**c**)

molecules was a prerequisite for high polymerization activity. The $_{1}$H-NMR (Fig. S2) and ^{13}C-NMR (Fig.S3) of the intermediate and ^{13}C-NMR (Fig. S4) of DCH are detailed in Supplementary Information. From the UV absorbance spectra of DSDA and DCH, there was a weak absorbance peak in the range of 230–240 nm, which was the UV absorbance peak of C=C. The maximum absorbance wavelength of DSDA was in the range of 320–330 nm. After modification with CC and HEA, the maximum absorbance wavelength of DCH appeared at 340–350 nm, which was also the maximum absorbance wavelength range of most fluorescent whitening agent stable structures. DSDA fluorescent whitening agents usually contain cis–trans-isomers, but the absorbance peak of the cis-structure of DCH was hardly observed. The reason for this might have been that HEA was long-linked to the ends of the triazine ring, such that the product had a certain spatial steric hindrance in the chemical spatial structure. This thus hindered the transformation of trans-isomer to cis-isomer and enhanced the stability of trans-isomers. Therefore, the UV absorbance intensity of trans-isomer was significantly greater than that of cis-isomer. The active component of DCH was the trans-isomer, which was fluorescent, whereas the cis-isomers were not [35]. By comparing the FT-IR spectra of DSDA and DCH, it was seen that they both had C=C stretching vibrations [36] and aromatic ring in-plane stretching vibrations [37] at 1620 cm^{-1} and 840–790 cm^{-1}. However, the DCH molecule also had C=O stretching vibrations [36] at 1720 cm^{-1} and a S=O stretching vibrations [36] at 1290–1280 cm^{-1}, which were characteristic functional groups in the DCH molecule.

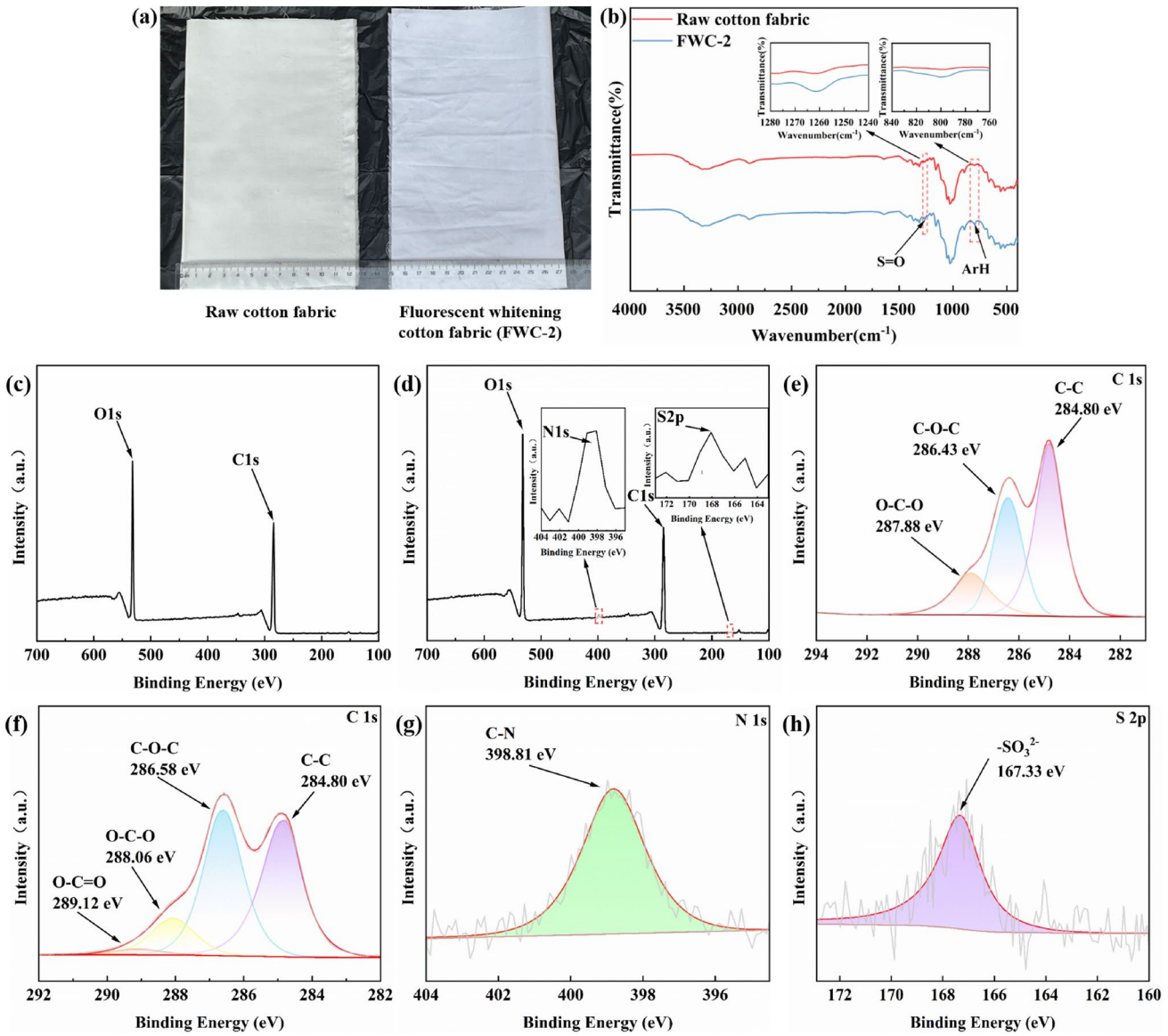

Fig. 5 (Color online) The raw cotton fabric and fluorescent whitening cotton fabric (FWC-2) in daylight (**a**), FT-IR spectra of raw cotton fabric and FWC-2 (**b**), XPS spectra of raw cotton fabric (**c**), XPS spectra of FWC-2(**d**), C-1 s XPS spectra of raw cotton fabric (**e**), and C-1 s, N-1 s, and S-2p XPS spectra of FWC-2 (**f**–**h**)

3.2 Characteristics of whitened cotton fabric

The good whitening effect of DCH on the raw cotton fabric was clearly seen with the naked eye in daylight (Fig. 5a). Compared with the FT-IR spectrum of the raw cotton fabric (Fig. 5b), FWC-2 showed that the S=O stretching vibrations [36] appeared at 1270–1250 cm^{-1} and aromatic ring in-plane stretching vibrations [37] at 840–790 cm^{-1}. The above functional groups are characteristic functional groups of the DCH structure, such that it was shown that DCH had been successfully grafted on raw cotton fabric.

To further demonstrate that DCH was grafted on the raw cotton fabric, X-ray photoelectron spectroscopy analysis (Fig. 5c–h) was performed on the raw cotton fabric and FWC-2. Only carbon, hydrogen and oxygen were observed on the raw cotton fabric, while there were not only carbon, hydrogen, and oxygen observed in the fabric, but also nitrogen and sulfur on the treated cotton fabric. The characteristic peaks of the C-1 s XPS spectrum at 284.8 eV, 286.47 eV, 288.27 eV, and 289.78 eV were attributed to C–C, C–O–C, O–C–O, and O–C=O [6]. The characteristic peak of N-1 s XPS spectrum at 398.81 eV belonged to C–N [38]. The characteristic peak of S-2p XPS spectrum at 167.33 eV belonged to SO_3^{2-} [39]. Therefore, it was shown that DCH molecules were grafted onto raw cotton fabric in the form of covalent bonds by electron beam irradiation grafting technology.

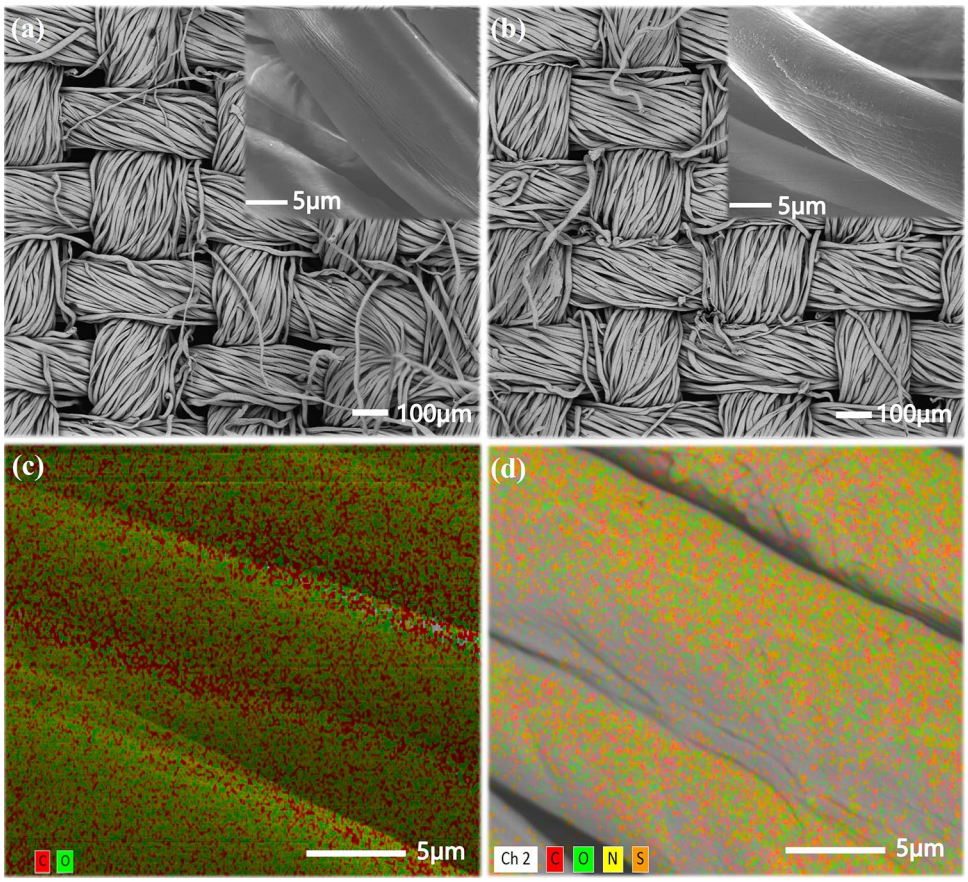

Fig. 6 (Color online) SEM images of the original cotton fabric (**a**) and FWC-2 (**b**), EDS mapping on original cotton fabric (**c**) and EDS mapping on FWC-2 (**d**)

Compared with the raw cotton fabric, the difference between the images before and after fabric modification was very small (Fig. 6a–b). The polymerized DCH could enter the cotton fabric in the form of small molecules, such that it had little effect on the surface morphology of the fabric, indicating that the influence of the modification process on the structure or surface morphology of the raw cotton fabric was negligible. EDS analysis was performed on the original cotton (Fig. 6c) and FWC-2 to explore the elemental changes on their surface. Results revealed that the distribution of nitrogen and sulfur confirmed uniform grafting of DCH onto the raw cotton fabric surface (Fig. 6d). Specific elemental content is detailed in Supplementary Information (Fig. S5).

3.3 Utilization of the fluorescent whitening agent

In the traditional textile dyeing and finishing process, the principle of fluorescent whitening agent for finishing raw cotton fabric is similar to that of direct dyes but that for polyester is similar disperse dye [40]. They bind to raw cotton fibers through weaker chemical bonds, such as van der Waals forces and hydrogen bonds. Therefore, this process has a low utilization rate of dyes. Compared with the utilization rate (60−70%) of traditional fluorescent whitening processes, the present utilization rate of DCH was close to 100% using electron beam irradiation grafting technology (Fig. 7a). The whiteness of the raw cotton fabric without whitening finishing was 74.50. DCH exhibited a good whitening effect on raw cotton fabric (Fig. 7b). With increased applied DCH concentration on the fabric, the blue-purple fluorescence intensity emitted by it also increased. When the concentration of whitening agent on the fabric increased to a suitable concentration, the blue-purple fluorescence emitted an offset yellow light on the fabric and the fabric whitening effect the best. As the concentration continues to increase, its own pale yellow will appear which caused the whitening effect to decrease [41]. At low concentration, the whiteness value increased with increased DCH concentration. When the concentration was greater than 0.3 wt%, the whiteness began to decrease. Therefore, the optimal DCH concentration was 0.3 wt%, with the fluorescent whitening effect the best and whiteness value the highest (110.81). In the concentration range of 1 wt%, the whiteness values were much higher than the raw cotton fabric whiteness. Compared with the raw cotton fabric, DCH-treated cotton fabric had an absorbance peak at 390 nm and absorbance increased with increased DCH concentration (Fig. 7c). According to the UV absorbance spectrum of DCH (Fig. 4b), the maximum absorption wavelength of DCH was 350 nm. This red

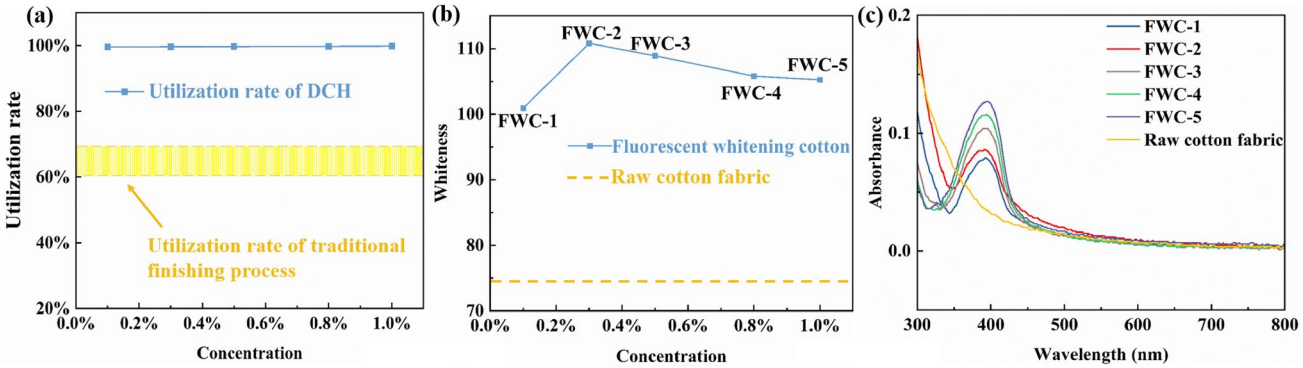

Fig. 7 (Color online) The utilization rate of DCH vs. concentration (a), whiteness of FWC fabric vs. DCH concentration (b), and UV–Vis absorbance of FWC fabrics and raw cotton fabric (c)

shift phenomenon is attributed to the interaction between cotton fabric macromolecules and fluorescent whitening agent molecules [42]. This also showed that DCH was successfully dyed onto the surface of raw cotton fabric and the blue-purple fluorescence reflected by absorbing UV light, thus offsetting the yellow color of the raw cotton fabric and finally achieving the effect of fluorescent whitening.

3.4 Washing and lighting durability

As mentioned above, traditional fluorescent whitening agents are combined with cotton fibers by weak chemical bonds, such that the finished products usually have low washing durability. However, the present fluorescent whitening finishing of cotton fabric was carried out by electron beam irradiation grafting technology, such that covalent bonds between the two gave it excellent washing fastness. According to the results of washing fastness tests of FWC-2, the change curve of whiteness with the number of accelerated laundering cycles was drawn (Fig. 8b). With increased number of accelerated laundering cycles, the whiteness of FWC-2 hardly changed (Fig. 8a). The UV–Vis absorbance spectra of FWC-2 before and after accelerated laundering cycles showed that the absorbance of washed cotton fabric did not change much before and after washing (Fig. 8c). Even under the condition of 20 accelerated laundering cycles (equivalent to 100 household washings), whiteness still remains above 110, demonstrating excellent color fastness to washing (with a color fastness grade of 5). For comparison, we used a commonly used fluorescent whitening agent, C186 (Fig. S6) to whiten cotton fabric via the traditional finishing process. It was found that the color fastness grade of the C186 whitened cotton fabric was only 1-2 [43] (Table 2). This means that it is very easily washed away, thereby greatly reducing the fluorescent whitening effect and the migration of fluorescent whitening agents might lead to environmental pollution and biosafety risks. Under sunlight, fluorescent whitening agent molecules can produce a photoisomerization phenomenon and the planar trans-structure can be transformed into a nonplanar cis-structure, thus losing fluorescence effect. The traditional finishing process makes the fluorescent whitening agent and cotton fiber combine with weak chemical bonds, which reduces the torsion performance of the stilbene structure and inhibits the process of cis-trans isomerization. However, with increased sun exposure time, the effect of fluorescent whitening also decreases significantly [44]. Herein, the light fastness of FWC-2 was also tested and the results showed that light fastness was better than grade of 4. The light fastness of C186 whitened cotton fabric was only 1-2 [43] (Table 2). As a result, DCH also showed excellent light durability. The reason for this was that the electron beam irradiation grafting technology enabled DCH molecules to be firmly covalently bonded to the raw cotton fabric, which improved the excellent light durability of the finished cotton fabric.

3.5 Skin safety

The combination of fluorescent whitening agent with cotton fiber by weak chemical bond also leads to its increased mobility. Therefore, the safety of a fluorescent whitening agent has always been a focus of discussion. As a fluorescent whitening agent used in textile cotton, its skin irritation experimentation is inevitable. Here, the covalently fluorescent whitening agent on the raw cotton fabric played a positive role. FWC-2 samples were used to test the skin irritation of New Zealand white rabbits. The skin response of New Zealand white rabbits was observed (Fig. 9), and the primary irritation index (PII) of all experimental groups was 0 (Table 3). No abnormal clinical symptoms except skin reaction were found in all animals, which showed that FWC-2 had no irritation to the surface of mammalian skin and met the safety standards of textiles. The specific experimental

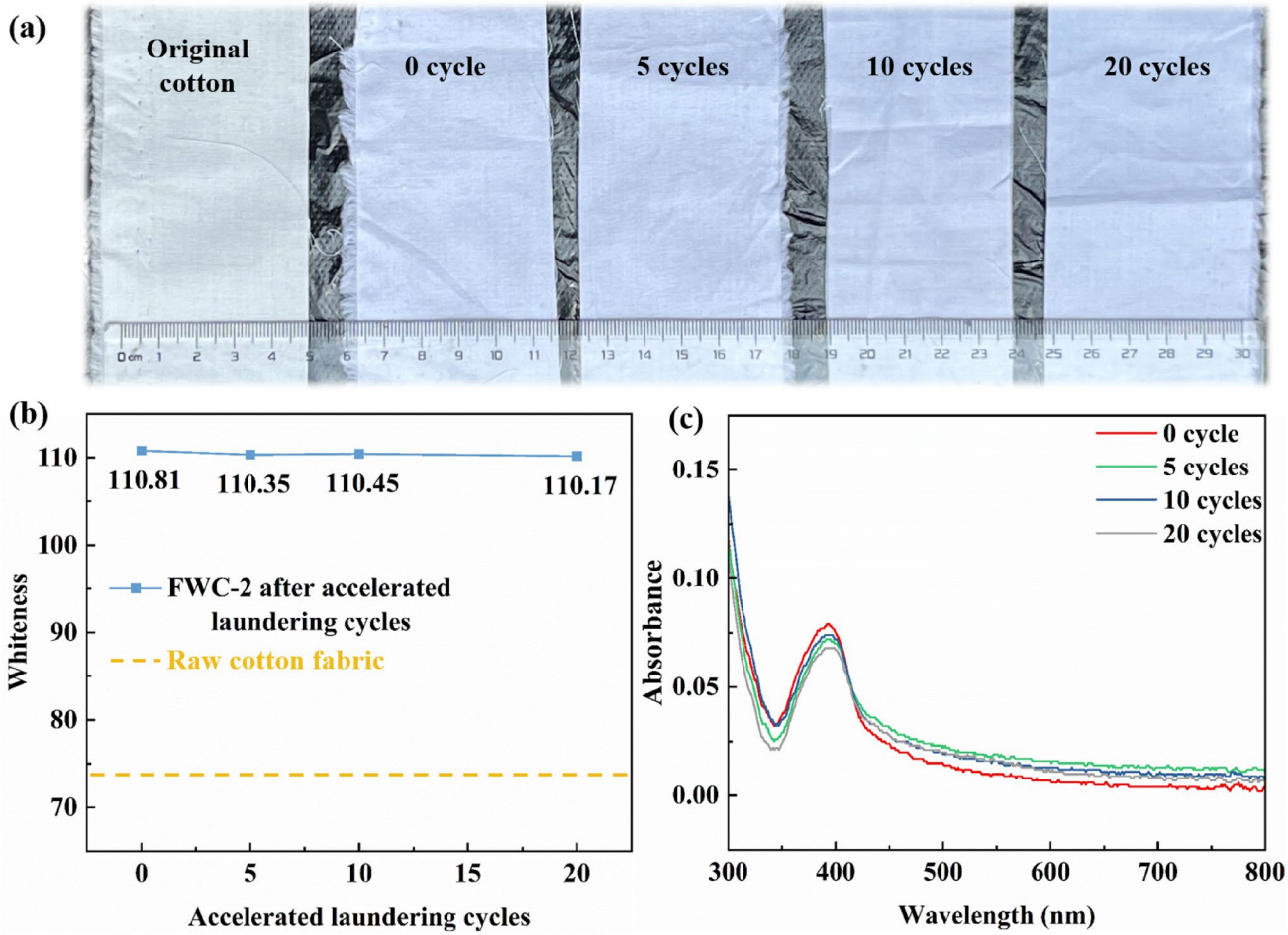

Fig. 8 (Color online) Photographs of FWC-2 before and after accelerated laundering (took under daylight) (a), whiteness value (b) and UV–Vis absorbance (c) of FWC-2 before and after accelerated laundering

Table 2 Rank of washability and light durability

Sample	Washing durability rank	Lighting durability rank
FWC-2	5	4–5
C186	1–2	1–2

details and evaluation criteria are listed in Supplementary Information (Table S1-S6). Here, the feasibility was shown for using DCH for fluorescent whitening finishing of cotton fabric by electron beam irradiation grafting technology and also provided an important basis for its industrialization.

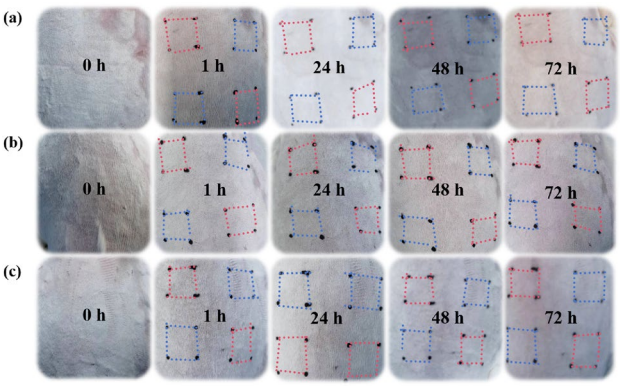

Fig. 9 Images are rabbits' back of the three groups contacting FWC-2 (in the circles marked with red-dotted lines) and negative control (in the circles marked with blue-dotted lines) at 0, 1, 24, 48, and 72 h

3.6 Energy and water consumption

In the process of fluorescent whitening via electron beam irradiation, the consumption of energy is almost exclusively generated by electron accelerator devices. The dose of 10 kGy meant that 1 kg of irradiated material absorbs 10 kJ of energy and the energy utilization rate of the electron accelerator device is not less than 80% [28]. The energy

Table 3 Method for fluorescent whitening of cotton fabric by electron beam irradiation

Animal No.	Dosing zone	Skin reaction	Interval (hours)				Average score
			1 ± 0.1	24 ± 2	48 ± 2	72 ± 2	
1	Test site (Left)	Erythema	0	0	0	0	0
		Edema	0	0	0	0	
	Test site (Right)	Erythema	0	0	0	0	
		Edema	0	0	0	0	
	Negative site (Left)	Erythema	0	0	0	0	0
		Edema	0	0	0	0	
	Negative site (Right)	Erythema	0	0	0	0	
		Edema	0	0	0	0	
2	Test site (Left)	Erythema	0	0	0	0	0
		Edema	0	0	0	0	
	Test site (Right)	Erythema	0	0	0	0	
		Edema	0	0	0	0	
	Negative site (Left)	Erythema	0	0	0	0	0
		Edema	0	0	0	0	
	Negative site (Right)	Erythema	0	0	0	0	
		Edema	0	0	0	0	
3	Test site (Left)	Erythema	0	0	0	0	0
		Edema	0	0	0	0	
	Test site (Right)	Erythema	0	0	0	0	
		Edema	0	0	0	0	
	Negative site (Left)	Erythema	0	0	0	0	0
		Edema	0	0	0	0	
	Negative site (Right)	Erythema	0	0	0	0	
		Edema	0	0	0	0	

consumption of the new method was calculated based on the absorbed dose and energy utilization rate of the electron accelerator device and found to be 12.5 kJ kg^{-1}. A simple calculation for the energy consumption of traditional finishing of 1 kg of cotton fabric was made, taking into account the energy required for heating water and maintaining the finishing vat temperature. Assuming the need to heat water from 20 °C to the typical process temperature of 50 °C and the specific heat capacity of water as 4.18 J g^{-1} °C^{-1}, the energy Q required to heat 1 kg of water was calculated using Eq. (3)

$$Q = c \times m \times \triangle t \tag{3}$$

where c is the specific heat capacity of water, m is the mass of water, and Δt is the temperature difference. Just heating the water would require 125.4 kJ kg^{-1} of energy. Next, the energy consumption required to maintain the finishing vat temperature was considered. According to a liquor ratio of 1/10, there is a total of 10 kg of water and 1 kg of cotton fabric in the finishing vat. Assuming that maintaining the temperature requires 10% of the energy used for heating [45], the energy consumption E to maintain the finishing vat temperature was calculated using Eq. (4)

$$E = Q \times m \times 10\% \tag{4}$$

where Q is the energy required to heat the water, and m is the total mass in the finishing vat. Thus, maintaining the finishing vat temperature would require 137.94 kJ of energy. Therefore, the total energy required for the traditional process of whitening 1 kg of cotton fabric through heating and maintaining temperature is 263.34 kJ. This amount is 21 times the energy consumption of treating 1 kg of cotton fabric with fluorescent whitening using radiation grafting technology. (This calculation is based on a simplified model, and the actual energy consumption might be affected by factors, such as the complexity of the finishing process and equipment efficiency.) In addition, after the traditional fluorescent whitening process, a curing and fixing operation is required to ensure the fixation of the fluorescent whitening agent on the cotton fabric and the durability of the fabric. This step typically requires a higher temperature [46]. The fluorescent whitening finishing process of textiles has become one of the most water-consuming industries. A close analysis of

the finishing process reveals that, in traditional fluorescent whitening, the water consumption is mainly concentrated in the post-treatment fabric washing process. Due to the lower utilization rate of fluorescent whitening agents, a large amount of fluorescent whitening agents, which have not been completely fixed to the cotton fabric, are absorbed on the surface of the fabric. If these fluorescent whitening agents are not thoroughly washed off, they might come off during the wearing process or affect the color fastness test results of the product. Traditional finishing processes require at least 5–10 washes. In contrast, in the case of the electron beam irradiation-induced fluorescent whitening process, due to the close to 100% utilization rate of fluorescent whitening agent, very few unfixed fluorescent whitening agents are attached to the fiber surface. Therefore, this process requires only one wash. Through calculation, it was estimated that the electron beam grafting finishing process can save at least 60 L of water per kilogram of cotton fabric in the fluorescent whitening agent process. To understand the pollution of the wastewater produced by this process, COD and electrical conductivity tests were performed on the wastewater from the electron beam irradiation-induced fluorescent whitening process (Table 4). Compared with that from the traditional finishing process (obtained from a textile dyeing plant of Shengtai Group, China), both the COD and conductivity values of the wastewater from the electron beam irradiation-induced fluorescent whitening process were much lower than the traditional finishing process, which means that, with the use of electron beam irradiation grafting technology for fluorescent whitening finishing, the organic matter and salt content in the wastewater reached the direct discharge standard, thus greatly reducing the cost of sewage treatment (Fig. 10).

Table 4 Method for fluorescent whitening of cotton fabric by electron beam irradiation

Sample	COD (mg L^{-1})	Electrical conductivity ($\mu S\ cm^{-1}$)
Deionized water	0	0
Wastewater of FWC-2	22	56
Wastewater of traditional finishing process	5428	2010

4 Conclusion

In this study, a vinyl-containing fluorescent whitening agent was synthesized and used to whiten raw cotton fabric, achieving about 100% of utilization rate assisted by electron beam irradiation. The vinyl-containing fluorescent whitening agent was confirmed to be covalently grafted onto the surface of cotton fibers. After treatment, the whiteness value of fabric reached 110.81 from the 74.50 of the original fabric using the present whitening solution at 0.3 wt% concentration. Due to covalent bonding with fibers, the whitened fabric maintained 110+ of whiteness value, even after the equivalent of 100 domestic washing cycles. This also exhibited excellent light fastness with a grade of

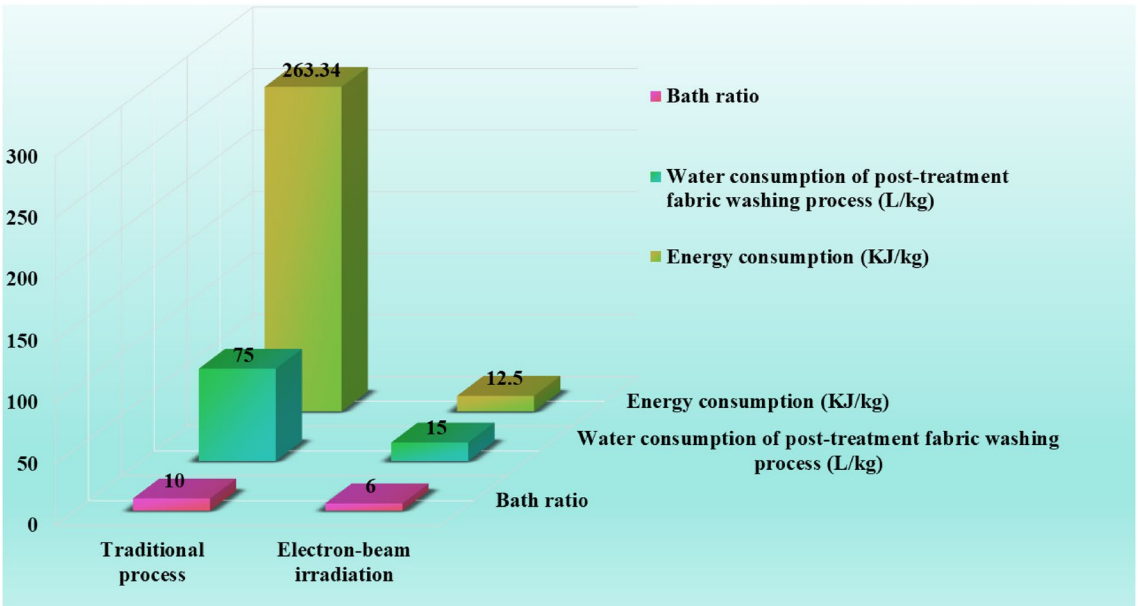

Fig. 10 (Color online) Comparison of energy consumption and water consumption of the electron beam irradiation-induced fluorescent whitening and traditional finishing process

4, demonstrating the good washing and lighting durability of the fluorescent whitening effect produced via electron beam irradiation. Skin irritation tests showed the whitened fabric caused 0 of the primary irritation index (PII) and no abnormal clinical symptoms, demonstrating its outstanding skin safety. The energy and water consumption of this process were also analyzed and found to require energy only 12.5 kJ kg^{-1} raw cotton fabric, which was much lower than the 263.34 kJ kg^{-1} required by the traditional process. The finishing wastewater generated from this process could save at least 180 L kg^{-1} of cotton fabric. In addition, the spent washing water of the above finishing process had such a low COD and electrical conductivity that they completely met the direct discharge of the wastewater, substantiating the energy conservation and pollution reduction characteristics of the electron beam irradiation-induced whitening method. All in all, this new fluorescent whitening finishing process via electron beam irradiation provided a green and sustainable pathway for development of the textile industry.

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Availability of data and materials The data that support the findings of this study are openly available in Science Data Bank at https://cstr.cn/31253.11.sciencedb.j00186.00670 and https://doi.org/10.57760/sciencedb.j00186.00670.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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