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

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Date: 2025-03-29T00:00:00+00:00

Abstract

Herein, a new method was developed for efficient and lasting fluorescent whitening of cotton fabric by synthesizing and using a vinyl-containing fluorescent whitening agent to covalently graft 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 was 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.

Full Text

Preamble

A Green Route to Covalently-Bonded Fluorescent Whitening of Cotton Fabric with Excellent Washing Durability and Skin Safety via Electron Beam Irradia-

tion

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Herein, we developed a new method for efficient and durable fluorescent whitening of cotton fabric by synthesizing a vinyl-containing fluorescent whitening agent that covalently grafts onto fiber surfaces with the assistance of electron beam irradiation. Analyses by FT-IR spectroscopy, X-ray photoelectron spectroscopy, and energy dispersive spectrometry confirmed that the fluorescent whitening agent was successfully anchored to cotton fibers via radiation-induced graft copolymerization. An optimized whiteness value of 110.81 was achieved (compared to 74.50 for raw cotton fabric) using just 0.3 wt% of the fluorescent whitening agent. Notably, the whiteness value of the treated cotton fabric remained above 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, with no abnormal clinical symptoms observed in any tested rabbits, demonstrating outstanding skin safety. Furthermore, the energy generated by the irradiation grafting technology was much lower than that of traditional processes, and water consumption was greatly reduced. The effluent from this process completely met industrial wastewater discharge standards 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

Introduction

With increasing demand for functionalization and aesthetics in textiles [1–5], fluorescent whitening agents have been widely used in textile finishing processes [6, 7]. Owing to noncovalent binding with textiles [8, 9], these agents typically exhibit low utilization in finishing processes (only 60–70%) [10] and are prone to wash-out during household laundry [8, 11, 12]. The effluents from textile finishing and washing contain difficult-to-treat fluorescent whitening agents [12–15], which are harmful to aquatic ecosystems and subsequently to human health [16–20]. Additionally, wash-out of fluorescent whitening agents from fabrics results in color deepening, reducing their market value. Therefore, efforts are necessary to improve both the finishing utilization and washing durability of

fluorescent whitening agents on fabrics.

High-energy radiation technology has proven to be a powerful tool in textile and fiber modification. Electron beams are used to treat difficult-to-degrade textile wastewater [21], and numerous novel functional fabric and fiber materials with superhydrophobicity [22–25], heavy metal ion and dye adsorption capabilities [26–29], antibacterial properties [30], antistatic properties [31], and photothermal properties [32–35] have been developed with the assistance of electron beam or gamma-ray irradiation. Recently, our group 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 [36–40]. As is well known, the covalent bonds (3–4 eV bond energy) in fiber chains are easily broken by high-energy radiation (1–5 MeV), generating free radicals on fibers that rapidly initiate graft polymerization of vinyl monomers. The covalent bonds between fibers and grafted segments contribute to permanent functionalization [41], which is why this novel dyeing method 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 [37, 40]. Besides that, this radiation-induced dyeing method significantly reduces the use of various finishing reagents in textile functional modification and offers low energy consumption, easy operation, and fast processing speed [42, 43]. Undoubtedly, this is an efficient and environmentally friendly textile processing method that could promote transformation of the traditional textile industry toward green and sustainable development.

Inspired by this approach, we synthesized 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), using 4,4' -diamino-2,2' -stilbenedisulfonic acid (DSDA), cyanuric chloride (CC), and hydroxyethyl methacrylate (HEA) as starting reagents. For brevity, we named this new fluorescent whitening agent DCH. We then used DCH to whiten raw cotton fabric with the assistance of electron beam irradiation, with the route summarized in Fig. 1. FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and energy dispersive spectrometry (EDS) were used to confirm successful 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 wash-durable and sunlight-durable fluorescent whitening effects. 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, wastewater from this electron beam irradiation-induced fluorescent whitening process was tested using COD and electrical conductivity meters to assess the content of residual organic matter and salts. This study provides a new low-pollution, low-energy-consumption textile finishing method superior to traditional chemical finishing methods, contributing to the transformation and upgrading of the textile industry.

[Figure 1: see original paper] Fig. 1 (Color online) Fluorescent whitening process of raw cotton fabric under electron beam irradiation.

Experimental

A. 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. Hydroxyethyl methacrylate (HEA, 300 mL), cyanuric chloride (CC, 50 g, 0.271 mol), and 4-hydroxy-2,2,6,6-tetramethylpiperidinooxy (4H-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, then additional DIPEA (50 mL, 0.287 mol) was added. The oil bath was heated to 30 °C for 2 h, and the reaction was monitored by thin layer chromatography (TLC). The organic phase was washed with water until the HEA was removed, then dried with anhydrous sodium sulfate, and ethyl acetate was 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-d_6) δ 6.35 (dd, J = 17.2, 1.6 Hz, 1H), 6.20 (dd, J = 17.3, 10.3 Hz, 1H), 5.97 (dd, J = 10.3, 1.6 Hz, 1H), 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 (10 mL), and 4H-TEMPO (0.086 g) were added and stirred until 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 an 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, HCl solution (0.2 M) was slowly added dropwise until a yellowish solid 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-d_6) δ 10.32 (s, 1H), 7.72 (dd, J = 8.6, 2.4 Hz, 1H), 6.36 (dd, J = 17.3, 1.7 Hz, 1H), 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.

[Figure 2: see original paper] Fig. 2 (Color online) Synthetic route of DCH.

B. Fluorescent Whitening of Raw Cotton Fabric by Electron Beam Irradiation

Raw cotton fabric (25 cm × 15 cm) was thoroughly washed with plenty of deionized water and then dried in a drying oven. DCH solutions with specific concentrations were prepared by rigorous stirring at room temperature, with HEA and N,N' -methylenebisacrylamide (MBA) added as auxiliary ingredients. The dried cotton fabric was fully immersed in the solution, then passed through a cotton fabric ginning machine (Fig. S1) at 1 bar pressure and 2 m min^{-1} speed to press the fabric. This squeezed the DCH solution into the gaps of the fabric and removed excess solution, ensuring even distribution of DCH 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) with an absorbed dose of 10 kGy at room temperature. After irradiation, the treated cotton fabric was washed in deionized water (60 times the sample mass) at 90 °C for 3 min, then dried in a vacuum oven at 60 °C. The spent washing water was collected and tested using COD and electrical conductivity meters. A series of whitened samples were prepared by adjusting the concentration of the fluorescent whitening solution (Table 1) and designated as FWC fabric.

The utilization rate can be calculated by Eq. 1:

$$\text{Utilization Rate } (\%) = \frac{n_w A_w}{n_0 A_0} \times 100\%$$

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

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

C. Whiteness Measurements

Fluorescent whitening samples were measured using a Datacolor 800 spectrophotometer (Technical Color Solutions, USA), with untreated cotton fabric used as the reference. A D65 light source was selected as the test light source. Each sample was measured three times on any fabric surface, and the average whiteness was recorded. Fluorescent whitening textiles typically use 3–4 level blue wool standard sample test levels; the 4-level blue wool standard sample test level was used in this test.

D. Skin Safety Test

Three healthy adult female (non-pregnant, nulliparous) New Zealand white rabbits were selected for skin safety testing. The samples were fluorescent whitening cotton fabric and blank gauze. Within 24 h before administration, hair was

removed from both sides of each animal' s back. The hair removal area was approximately 10 cm × 15 cm to meet application needs (Fig. 3). The sample was cut into small pieces (2.5 cm × 2.5 cm) and directly attached to the corresponding depilated skin, then covered with a layer of cellophane and four layers of gauze, and finally sealed and bandaged with medical tape. After 4 h of application, the sample was removed and the administration site marked with an oily marker pen. Residual sample on the skin was washed with warm water and dried. Blank gauze was applied to the control site using the same procedure. Erythema and edema reactions of the animal skin were observed at 1 ± 0.1 h, 24 ± 2 h, 48 ± 2 h, and 72 ± 2 h after patch removal. Scores were evaluated according to the observation results, and the primary irritation index (PII) was calculated according to Eq. 2:

$$\mathrm{PII} = \frac{\sum A}{n_1} - \frac{\sum N}{n_2}$$

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

[Figure 3: see original paper] Fig. 3 (Color online) Location of skin application sites: Cranial end (1), test site (2), negative control site (3), clipped dorsal region (4), and caudal end (5).

E. Washing and Light Fastness Test

The fluorescent whitening sample was cut to 50 mm × 150 mm. To evaluate washing fastness, an accelerated washing durability test was carried out according to AATCC61-2006 test method (condition 2A), where one accelerated washing cycle equals five home washing cycles. The washed cotton fabric was rinsed with distilled water at 40 °C and dried at 60 °C. Fluorescent whitening samples were measured using the Datacolor 800 spectrophotometer, and the whiteness change curve was plotted against washing cycles.

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

Results and Discussion

A. Structural Analysis of DCH

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

high proportion of vinyl groups in DCH 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 the Supplementary Information. The UV absorbance spectra of DSDA and DCH showed a weak absorbance peak in the 230–240 nm range, corresponding to the UV absorbance of C=C bonds. The maximum absorbance wavelength of DSDA was in the 320–330 nm range. After modification with CC and HEA, the maximum absorbance wavelength of DCH appeared at 340–350 nm, which is also the typical range for stable fluorescent whitening agent structures. DSDA fluorescent whitening agents usually contain cis-trans isomers, but the absorbance peak of the cis-structure of DCH was hardly observed. This may be because HEA formed long linkages at the ends of the triazine ring, creating spatial steric hindrance in the chemical structure that hindered transformation from trans- to cis-isomer and enhanced stability of the trans-isomer. Therefore, the UV absorbance intensity of the trans-isomer was significantly greater than that of the cis-isomer. The active component of DCH was the trans-isomer, which is fluorescent, whereas cis-isomers are not [44]. Comparing the FT-IR spectra of DSDA and DCH, both showed C=C stretching vibrations [45] and aromatic ring in-plane stretching vibrations [46] at 1620 cm^{-1} and 840–790 cm^{-1}. However, the DCH molecule also exhibited C=O stretching vibrations [45] at 1720 cm^{-1} and S=O stretching vibrations [45] at 1290–1280 cm^{-1}, which are characteristic functional groups in the DCH molecule.

[Figure 4: see original paper] 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).

B. Characteristics of Whitened Cotton Fabric

The good whitening effect of DCH on raw cotton fabric was clearly visible to the naked eye in daylight (Fig. 5a). Compared with the FT-IR spectrum of raw cotton fabric (Fig. 5b), FWC-2 showed S=O stretching vibrations [45] at 1270–1250 cm^{-1} and aromatic ring in-plane stretching vibrations [46] at 840–790 cm^{-1}. These functional groups are characteristic of the DCH structure, confirming that DCH had been successfully grafted onto raw cotton fabric.

To further demonstrate DCH grafting, X-ray photoelectron spectroscopy analysis was performed on raw cotton fabric and FWC-2 (Figs. 5c–h). Only carbon, hydrogen, and oxygen were observed on raw cotton fabric, while nitrogen and sulfur were additionally detected on the treated cotton fabric. The characteristic peaks of the C 1s 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 bonds [10]. The characteristic peak of the N 1s XPS spectrum at 398.81 eV belonged to C–N bonds [47]. The characteristic peak of the S 2p XPS spectrum at 167.33 eV belonged to SO_3^{2-} [48]. These results demonstrated that DCH molecules were grafted onto raw cotton fabric via covalent bonds through electron beam irradiation grafting technology. SEM images showed minimal difference between raw

cotton fabric and FWC-2 (Figs. 6a–b). The polymerized DCH could penetrate the cotton fabric as small molecules, having little effect on fabric surface morphology and indicating that the modification process had negligible influence on the structure or surface morphology of raw cotton fabric. EDS analysis was performed on original cotton (Fig. 6c) and FWC-2 to explore elemental changes on their surfaces. Results revealed uniform distribution of nitrogen and sulfur, confirming uniform grafting of DCH onto the raw cotton fabric surface (Fig. 6d). Specific elemental content is detailed in the Supplementary Information (Fig. S5).

[Figure 5: see original paper] Fig. 5 (Color online) 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 1s XPS spectra of raw cotton fabric (e), and C 1s, N 1s, and S 2p XPS spectra of FWC-2 (f–h).

[Figure 6: see original paper] Fig. 6 (Color online) SEM images of original cotton fabric (a) and FWC-2 (b), EDS mapping on original cotton fabric (c) and EDS mapping on FWC-2 (d).

C. Utilization of the Fluorescent Whitening Agent

In traditional textile dyeing and finishing processes, fluorescent whitening agents bind to raw cotton fibers through weaker chemical bonds such as van der Waals forces and hydrogen bonds, similar to direct dyes (while for polyester they behave like disperse dyes) [49]. Consequently, these processes have low dye utilization rates. Compared with the 60–70% utilization rate of traditional fluorescent whitening processes, the utilization rate of DCH approached nearly 100% using electron beam irradiation grafting technology (Fig. 7a). The whiteness of raw cotton fabric without whitening finishing was 74.50. DCH exhibited good whitening effects on raw cotton fabric (Fig. 7b). As the applied DCH concentration on the fabric increased, the blue-purple fluorescence intensity also increased. When the whitening agent concentration reached an optimal level, the blue-purple fluorescence offset the yellow light on the fabric, producing the best whitening effect. As concentration continued to increase, the inherent pale yellow color appeared, causing the whitening effect to decrease [50]. At low concentrations, whiteness values increased with DCH concentration, but when concentration exceeded 0.3 wt%, whiteness began to decrease. Therefore, the optimal DCH concentration was 0.3 wt%, producing the best fluorescent whitening effect and highest whiteness value (110.81). Within the 1 wt% concentration range, all whiteness values were much higher than that of raw cotton fabric. Compared with raw cotton fabric, DCH-treated cotton fabric showed an absorbance peak at 390 nm, with absorbance increasing as DCH concentration increased (Fig. 7c). According to the UV absorbance spectrum of DCH (Fig. 4b), the maximum absorption wavelength of DCH was 350 nm. This red shift phenomenon is attributed to interaction between cotton fabric macromolecules and fluorescent whitening agent molecules [51], further confirming that DCH

was successfully dyed onto the surface of raw cotton fabric. The blue-purple fluorescence reflected by absorbing UV light offset the yellow color of raw cotton fabric, finally achieving the fluorescent whitening effect.

[Figure 7: see original paper] 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).

D. Washing and Light Durability

As mentioned above, traditional fluorescent whitening agents combine with cotton fibers through weak chemical bonds, resulting in low washing durability. However, the present fluorescent whitening finishing of cotton fabric was achieved through electron beam irradiation grafting technology, where covalent bonds between the agent and fiber provided excellent washing fastness. According to washing fastness test results for FWC-2, the whiteness change curve was plotted against the number of accelerated laundering cycles (Fig. 8b). As the number of accelerated laundering cycles increased, the whiteness of FWC-2 hardly changed (Fig. 8a). UV-Vis absorbance spectra of FWC-2 before and after accelerated laundering cycles showed minimal absorbance changes (Fig. 8c). Even after 20 accelerated laundering cycles (equivalent to 100 household washings), whiteness remained above 110, demonstrating excellent color fastness to washing (with a color fastness grade of 5). For comparison, we whitened cotton fabric using a commonly employed fluorescent whitening agent, C186 (Fig. S6), via the traditional finishing process. The color fastness grade of C186-whitened cotton fabric was only 1–2 [52] (Table 2), meaning it is easily washed away, greatly reducing the fluorescent whitening effect and potentially causing environmental pollution and biosafety risks through migration of the whitening agent.

Under sunlight, fluorescent whitening agent molecules can undergo photoisomerization, where the planar trans-structure transforms into a nonplanar cis-structure, thus losing fluorescence effect. The traditional finishing process forms weak chemical bonds between the fluorescent whitening agent and cotton fiber, reducing torsion performance of the stilbene structure and inhibiting the cis-trans isomerization process. However, with increased sun exposure time, the fluorescent whitening effect decreases significantly [53]. Herein, the light fastness of FWC-2 was also tested, showing a grade better than 4. In contrast, the light fastness of C186-whitened cotton fabric was only 1–2 [52] (Table 2). Therefore, DCH also exhibited excellent light durability because electron beam irradiation grafting technology enabled DCH molecules to be firmly covalently bonded to raw cotton fabric.

[Figure 8: see original paper] Fig. 8 (Color online) Photos of FWC-2 before and after accelerated laundering (taken 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

E. Skin Safety

The combination of fluorescent whitening agents with cotton fiber through weak chemical bonds also increases their mobility, making safety a constant focus of discussion. Skin irritation experimentation is essential for fluorescent whitening agents used in textile cotton. Here, the covalently bonded fluorescent whitening agent on raw cotton fabric played a positive role. FWC-2 samples were used to test skin irritation in New Zealand white rabbits. Skin responses were observed (Fig. 9), and the primary irritation index (PII) of all experimental groups was 0 (Table 3). No abnormal clinical symptoms except skin reactions were found in any animals, showing that FWC-2 caused no irritation to mammalian skin surfaces and met textile safety standards. Specific experimental details and evaluation criteria are listed in the Supplementary Information (Tables S1–S6). These results demonstrate the feasibility of using DCH for fluorescent whitening finishing of cotton fabric by electron beam irradiation grafting technology and provide an important basis for its industrialization.

[Figure 9: see original paper] Fig. 9 Images of rabbits' backs from the three groups contacting FWC-2 (in circles marked with red-dotted lines) and negative control (in circles marked with blue-dotted lines) at 0, 1, 24, 48, and 72 h.

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

F. Energy and Water Consumption

In the electron beam irradiation fluorescent whitening process, energy consumption is generated almost exclusively by the electron accelerator device. A dose of 10 kGy means 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% [35]. The energy consumption of the new method was calculated based on the absorbed dose and energy utilization rate of the electron accelerator device, yielding 12.5 kJ kg^{-1}. A simple calculation for energy consumption of traditional finishing of 1 kg of cotton fabric was made, considering energy required for heating water and maintaining finishing vat temperature. Assuming water must be heated from 20 °C to the typical process temperature of 50 °C, with water' s specific heat capacity of 4.18 J g^{-1} $°C^{-1}$, the energy Q required to heat 1 kg of water was calculated using Eq. 3:

$$Q = c \times m \times \Delta t$$

where c is the specific heat capacity of water, m is the mass of water, and Δt is the temperature difference. Heating the water would require 125.4 kJ kg^{-1} of energy. Next, energy consumption 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 temperature requires 10% of the energy used for heating [54], the energy

consumption E to maintain finishing vat temperature was calculated using Eq. 4:

$$E = Q \times m \times 10\%$$

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 temperature maintenance 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 actual energy consumption might be affected by factors such as process complexity and equipment efficiency).

In addition, after the traditional fluorescent whitening process, a curing and fixing operation is required to ensure fixation of the fluorescent whitening agent on cotton fabric and durability of the fabric. This step typically requires higher temperatures [55]. The fluorescent whitening finishing process of textiles has become one of the most water-consuming industries. Detailed analysis reveals that in traditional fluorescent whitening, water consumption is concentrated in the post-treatment fabric washing process. Due to the lower utilization rate of fluorescent whitening agents, large amounts of unfixed agents remain adsorbed on the fabric surface. If not thoroughly washed off, these agents might detach during wear or affect product color fastness test results. Traditional finishing processes require at least 5–10 washes. In contrast, the electron beam irradiation-induced fluorescent whitening process, with its near-100% utilization rate, has very few unfixed fluorescent whitening agents attached to the fiber surface, requiring only one wash. Through calculation, we 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 process.

To assess pollution from process wastewater, COD and electrical conductivity tests were performed on wastewater from the electron beam irradiation-induced fluorescent whitening process (Table 4). Compared with wastewater from the traditional finishing process (obtained from a textile dyeing plant of Shengtai Group, China), both COD and conductivity values were much lower, meaning that with electron beam irradiation grafting technology for fluorescent whitening finishing, organic matter and salt content in wastewater reached direct discharge standards, greatly reducing sewage treatment costs.

[Figure 10: see original paper] Fig. 10 (Color online) Comparison of energy consumption and water consumption between electron beam irradiation-induced fluorescent whitening and traditional finishing processes.

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

Conclusions

In this study, a vinyl-containing fluorescent whitening agent was synthesized and used to whiten raw cotton fabric, achieving approximately 100% utilization rate with the assistance of electron beam irradiation. The vinyl-containing fluorescent whitening agent was confirmed to be covalently grafted onto the surface of cotton fibers. After treatment, the fabric whiteness value reached 110.81 (from 74.50 for the original fabric) using a 0.3 wt% whitening solution. Due to covalent bonding with fibers, the whitened fabric maintained a whiteness value above 110 even after the equivalent of 100 domestic washing cycles. The fabric also exhibited excellent light fastness with a grade of 4, demonstrating good washing and light durability of the fluorescent whitening effect produced via electron beam irradiation. Skin irritation tests showed the whitened fabric caused a primary irritation index (PII) of 0 with no abnormal clinical symptoms, demonstrating outstanding skin safety. Energy and water consumption analysis revealed the process required only 12.5 kJ kg^{-1} for raw cotton fabric, much lower than the 263.34 kJ kg^{-1} required by traditional processes. The finishing wastewater could save at least 180 L kg^{-1} of cotton fabric. Additionally, the spent washing water from this finishing process had such low COD and electrical conductivity that it completely met direct discharge wastewater standards, substantiating the energy conservation and pollution reduction characteristics of the electron beam irradiation-induced whitening method. Overall, this new fluorescence whitening finishing process via electron beam irradiation provides a green and sustainable pathway for development of the textile industry.

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Note: Figure translations are in progress. See original paper for figures.