Effluent-free deep dyeing of cotton fabric with cacao husk extracts using the Taguchi optimization method

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Abstract

Textile dyehouses are under scrutiny because they discharge colored and hazardous effluents to waterways. There is a need to develop an alternative dyeing system that does not produce any hazardous effluent. The waterless dyeing method could be a viable eco-friendly alternative to the traditional aqueous dyeing method. In this work, cacao husk extracts were used as a natural dye in the decamethylcyclopentasiloxane (D5) medium for the dyeing of cotton fabric, and subsequently, the dyed cotton was treated by a fixation treatment with a cationic dye-fixing agent in the D5 medium. The cotton fabric dyed with cacao husk extracts exhaustion in the waterless D5 medium exhibited better exhaustion, fixation rate, color strength (K/S), and colorfastness to washing and rubbing compared to the fabric dyed with the same extracts using the conventional aqueous dyeing and dye-fixing methods. The dye exhaustion percentage and the dye fixation rate were 95.6% and 94.8% in the D5 medium respectively, which is significantly higher in comparison to a 48.2% dye exhaustion percentage and a 35.3% dye fixation rate in the conventional water medium. An orthogonal array design (L9) was adopted to optimize the dyeing conditions with respect to exhaustion percentage. The results indicated that the dyebath temperature was the most important factor for achieving the optimal dye exhaustion, and dyeing time also showed considerable effects. Linear regression was used to predict the exhaustion percentage, and the resulting p value of 0.000 demonstrated that a strong coefficient was proven among all selected factors. This study has demonstrated that dyeing of cotton fabric with cacao husk extracts in the D5 dyeing system can be a viable method for the textile industry with minimal environmental pollution.

Introduction

Traditional dyeing of cellulosic fabrics with reactive dyes produces strongly colored effluent laden with high amounts of hydrolyzed reactive dyes, salts, and other chemical auxiliaries (Cai et al. 2018; Su et al. 2019). As a result, this effluent cannot be discharged into watercourses without supplemental treatments. Generally, textile dyeing is carried out in a water-based dyebath system because the dyes are soluble in water and the fibers swell in water, which facilitates the transport of dye molecules from the dyebath to the interior of the fiber (Fu et al. 2013; Toprak et al. 2018). The effluent generated by a reactive dyeing method is still a major concern because it seriously affects human health and the ecosystem (Ali et al. 2014; Pervez and Stylios 2018b; Pervez et al. 2020). Therefore, innovative and sustainable methods reducing water consumption and producing minimal or zero effluents are highly attractive for textile dyeing industries.

Based on environmental concerns and the high cost of treatment of the discharged effluent, the application of natural dyes has gained popularity as a cleaner alternative to harmful synthetic dyes (Benli and Bahtiyari 2015; Davulcu et al. 2014; Habib et al. 2017). Recently, several journal articles have been published that report the dyeing and functionalization of cotton fabric with natural dyes providing many functional properties including UV protection and antibacterial activity (Da Silva et al. 2018; Motaghi 2018; Pisitsak et al. 2018). In all studies, a traditional aqueous exhaustion dyeing method was used, which was unable to solve the fundamental problems of traditional dyeing mentioned previously, i.e., they are not effluent-free. In addition, the practical use of natural dyes is limited because of disadvantages such as difficulty in achieving deep colors/dark shades, limited availability, and poor colorfastness to washing, rubbing, and light (Li et al. 2016; Nakpathom et al. 2019). Therefore, the development of an effluent-free, environmentally friendly natural dyeing process with improved properties must be established for the sustenance of the textile dyeing industry.

In recent years, non-aqueous based dyeing technology has received considerable attention as an alternative to traditional aqueous exhaust dyeing systems. Various non-aqueous based dyeing technologies have been explored (Sawada and Ueda 2003; Yang et al. 2017). Of them, the reverse micelle dyeing system is considered as one of the most viable 123 518 Cellulose (2021) 28:517–532 techniques compared to other waterless dyeing methods (Lee et al. 2019; Tang et al. 2018). This system comprises an organic solvent and miscible fluids stabilized by surfactants and co-surfactants. Surfactants and co-surfactants can effectively reduce interfacial tension to form microemulsions (Salager et al. 2013) and create a 'water pool' where the water soluble dyes can be properly dispersed and form an effective emulsion between the dye solution and nonaqueous medium (Fig. 1) (Wang et al. 2016). Various hydrocarbon-based solvents such as n-heptane, hexane, cyclohexane, and isooctyl silane have been used as the continuous phase medium in the reverse micelle dyeing system, but these solvents are not environmentally friendly. As a result, the practical application of these dyeing systems in the textile industry is limited (Fu et al. 2015). Recently, decamethylcyclopentasiloxane (D5) has been chosen as a feasible continuous phase medium instead of alkane-based solvents in the reverse micelle dyeing system (Liu et al. 2012). D5 is a clear, colorless, odorless, and nonoily siloxane fluid (Tang et al. 2017), which has been envisaged as a safe solvent for humans and the environment (Fu et al. 2016). After the dyeing process, D5 can be separated from the aqueous part, which mainly consists of water, ethyl alcohol, and D5 and can be subsequently recycled and reused by a simple static separation (Pei et al. 2019).

Recently, several investigations have reported textile dyeing with synthetic dyes in a D5 dyeing system (Li et al. 2011; Pei et al. 2017), while little research has focused on textile fiber dyeing with natural dyes using the D5 solvent. Therefore, we have attempted to enhance the exhaustion of natural dyes by an innovative method using the D5 solvent. However, when dyeing cotton with natural dyes, metal ions are typically used to improve the performance by pre-mordanting dyeing, simultaneous dyeing, or post-mordanting dyeing. Thus, after exhaust dyeing of cotton fiber with natural dyes in a D5 medium, a fixation treatment is required to improve the dye fixation, wash fastness, and rubbing fastness. Here, the use of a traditional fixation method that applies a cationic fixation auxiliary solution to fix natural dyes by padding or the exhaustion method is unsuitable. This is because much of the physically adsorbed dye in the dyed fiber is immediately dissolved into the auxiliary aqueous solution during the fixation treatment, which results in a low fixation rate. These dissolved dyes into the auxiliary solution potentially stain the dyed fabrics during the fixation treatment, resulting in an uneven color problem. Besides, the usage of heavy metal salts as mordants are not only harmful to the environment but also present challenges with color stability, which is unsuitable for large-scale production and application (Amutha and Sudhapriya 2020; I˙s¸mal and Yıldırım 2019). Thus, after dyeing cotton fiber with natural dyes in a D5 medium, to be effective at fixing the natural dyes in the cotton fiber, a fixation treatment using an eco-friendly cationic auxiliary in a D5 medium is necessary. This research will encourage more waterless dyeing studies of textiles with other natural dyes to improve the sustainability of textile processing.

Generally, dyeing performance is influenced by various operational parameters and a set of welldesigned experiments are needed to determine a satisfactory dyeing process. In this case, the statistical modeling-based technique can be a viable option according to the literature. The Taguchi technique is such a method that can be applied to optimize the process conditions and simultaneously improve the process performance (Cai et al. 2020; Pervez et al. 2018; Rehman et al. 2015). The Taguchi method utilizes a signal to noise ratio (S/N) to obtain optimal conditions from the response table, and analysis of variance (ANOVA) tables are the primary sources for significance determination of the individual factor. Lately, a confirmation test has been employed to validate the design of experiments with respect to practical viability. The main advantage of this technique is that it can run all parameters at the same time, while the conventional optimization process only allows one parameter to change during the process, which is time-consuming and expensive. Hence, we adopted a Taguchi technique for the systematic optimization of the deep dyeing of cotton fabric with cacao husk extracts in a D5 medium, and to the best of the authors' knowledge, there is no report yet published on this until now.

The objective of the present work is to identify whether cacao husk extracts can be used as a natural dye in the D5-based, effluent-free dyeing process for dyeing cotton fabric and the production of high dye exhaustion via exhaust dyeing condition optimization. The experimental design was moduled on an orthogonal array (L9) with three parameters and three levels. Subsequently, the dyed cotton fabric was treated by a cationic fixation treatment in a D5 medium to achieve a deep shade and good colorfastnesses. The exhaustion dyeing parameters were systematically evaluated using a Taguchi statistical optimization technique (Cai et al. 2020; Pervez et al. 2018; Rehman et al. 2015). Moreover, the dyeability of cotton fabric in D5 solvent was compared with a conventional aqueous dyeing system to prove the suitability of this method over traditional dyeing processes.

Experimental Materials

In this work, a desized, bleached, and scoured 100% cotton plain-woven fabric of 140 g m^{-2} was received from Jiangnan Group Co., Ltd., China. The cacao husk extract was purchased from Organic Herb Inc., China, and used without further purification. Alkylalcoholpolyoxy-ethylene ether (AEO-3) surfactant was purchased from Chengdu Aikeda Chemical Reagent Co., Ltd., China. Decamethylcyclopentasiloxane (D5) was obtained from Jiangxi Bluestar Xinghuo Silicones Co., Ltd., China. N-octanol co-surfactant and ethyl alcohol were procured from Sinopharm Chemical Reagent Co., Ltd., Ningbo, China. A cationic fixation agent, ALBAFIX ECO, was purchased from Huntsman Chemicals, USA. All other chemicals and reagents were laboratory grade.

Taguchi method

The Taguchi method is considered one of the most common statistical approaches to evaluate the order of significance of several factors for a selected response (Simpson 1987). In the Taguchi method, orthogonal arrays of an experimental design are applied to a selected number of parameters resulting in the simultaneous reduction of cost and time compared to the full factorial experiments (Pervez and Stylios 2018a; Weissman and Anderson 2014). The main purpose of this system is to analyze the influence of different process parameters on the mean and variance data and 123 520 Cellulose (2021) 28:517–532 determine the most significant contributor to the variables. In the design of the process of the experiment, the output of each trial is observed based on the values of the signal to noise (S/N) ratio. In our model, a high S/N ratio is better, as is expressed in Eq. 1 (Fratila and Caizar 2011).

$$S/N = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \quad (1)$$

where yi is the ith experiment in the design of orthogonal array, and n represents the whole number of tests.

Exhaust dyeing procedure in a D5 medium

Initially, a predetermined amount of surfactant, AEO3, and co-surfactant, n-octanol, were mixed in a mass ratio of 1:1 with stirring at room temperature, where n-octanol was used to improve the solubility of AEO-3 in D5, and both the chemicals assisted in emulsifying the cacao husk extract solution in a D5 medium (Pei et al. 2017). A fixed amount (25 g L^{-1}) of the surfactant/co-surfactant mixture was then added to the D5 solution. Stirring continued until a homogeneous, stable, and transparent microemulsion was formed. Finally, a certain volume (2 mL) of the concentrated cacao husk extracts solution was slowly added to it, and the mixture was stirred until a stable cacao husk extracts/D5 microemulsion was formed. Then, 2.0 g of cotton fabric was inserted into the microemulsion at a liquor ratio of 1:20. Then, process parameters, including dyeing temperature (80–100 °C), dyeing time (80–100 min), and the applied dosage of cacao husk extracts (2–4% o.w.f) were varied. The dyeing process was performed in an infrared dyeing machine (Model: HB-HWX24, Ronggui Huibao Dyeing, and Finishing Machinery Factory, China). Dyes and other auxiliaries were added at room temperature (20 °C) and the dye bath was heated at 2 °C min-1 to the required temperature. Consequently, the experimental design was run based on the Taguchi model. Statistical software, Minitab@17, was used for the design of experiments. A total of nine experimental trials were adopted by selecting three factors and three levels, and the details are shown in Tables 1 and 2. Exhaust dyeing procedure in a water medium The control dyeing of cotton fabric was carried out in an aqueous medium with 2% o.w.f of cacao husk extracts at 80 °C for 90 min using a liquor ratio of 1:20 by using the same dyeing machine used for the waterless dyeing at the same dyeing conditions.

Thermal stability of cacao husk extracts

The cacao husk extracts/D5 microemulsion (0.04 g of cacao husk extracts in 40 mL) was heated in the dyeing machine at 60–100 °C for 100 min. To test thermal stability, 1 mL of the original and heated cacao husk extracts/D5 microemulsion were diluted to 25 mL by ethanol and then subsequently analyzed by the UV–Vis spectrophotometer.

Dye exhaustion

The exhaustion percentage was determined by measuring the concentration of cacao husk extracts in the dyebath before and after dyeing. The exhaustion percentage was measured by measuring the absorption of the dyebath solution before and after dyeing with a UV–Vis spectrophotometer (Model: TU-1900, PERSEE Analytics, China). The maximum absorption of the cacao husk extract was found to be at the wavelength 477 nm. In the case of the D5 dyeing processes, a predetermined amount of D5 dyebath solution was dissolved in ethyl alcohol to enable uniform dispersion of dye molecules and also to ensure an accurate light absorption measurement. The total amount of the cacao husk extracts exhaustion percentage (E%) was estimated with Eq. 2 (Al-Degs et al. 2009; Yang and Huda 2003).

$$E\% = \left(\frac{A_o - A_1}{A_o}\right) \times 100\% \qquad (2)$$

where A0 and A1 are the absorbances of the cacao husk extracts solution before and after dyeing, respectively.

Dye fixation treatment in D5 medium

After the exhaust dyeing of the cotton fabric under optimized conditions (2% o.w.f of cacao husk extracts at 80 °C for 90 min) using a liquor ratio of 1:20, the dyed sample was squeezed and dried at 80 °C for 30 min for the following dye fixation treatment. The fixation of the cacao husk extract dye with cotton fiber was carried out with a cationic dye-fixing agent in the D5 medium system. It is similar to the D5 dyebath, only the dye was replaced by the cationic dye-fixing agent. The dye fixation treatment was carried out in the dyeing machine using a liquor ratio of 1:20 at 80 C for 20 min. The dosage of the cationic dye-fixing agent was 5% o.w.f. After the fixation treatment, the dyed fabric was soaped off in a solution containing 2 g L-1 of a nonionic detergent (Luton 500, Dalton UK Company) using a liquor ratio of 1:20 at 95 °C for 15 min. After the soaping process, the residual soaping solution was diluted by ethyl alcohol, i.e. 5 mL to 25 mL, and that was used to measure the absorbance at 477 nm with the UV–Vis spectrophotometer. The fixation rate (F%) and total fixation percentage (T%) were calculated by Eqs. 3 and 4.

$$F\% = \left(\frac{A_o - A_1 - A_2}{A_o - A_1}\right) \times 100\% \qquad (3)$$

$$T\% = E\% \times F\% \times 100 \qquad (4)$$

where A2 is the absorbance of the residual soaping solution.

Dye fixation treatment in a water medium

After the exhaust dyeing of cotton fabric in a water medium and a D5 medium, the dyed fabrics were treated by a fixation treatment in the water medium. The dye fixation treatment was carried out in the dyeing machine using a liquor ratio of 1:20 with 5% o.w.f. of a cationic dye-fixing agent at 80 °C for 20 min. After the fixation treatment, the dyed fabric was soaped off in a solution containing 2 g L-1 of a nonionic detergent (Luton 500, Dalton UK Company) using a liquor ratio of 1:20 at 95 °C for 15 min. After the soaping process, the residual soaping solution was collected to measure the absorbance at 477 nm with the UV–Vis spectrophotometer. The fixation rate (F%) and total fixation percentage (T%) were again calculated by Eqs. 3 and 4.

Color strength and colorfastness test

The color strength (K/S) of the sample was measured using a reflectance spectrophotometer (CS-650A, Hangzhou Color Spectrum Technology Co. Ltd, China) measured on 20 random spots. The mean of these 20 K/S values was calculated to express the color strength of the sample. The colorfastness of the sample was tested according to the ISO standard test method (ISO 105-C06:1997), and the colorfastness to rubbing was tested according to the ISO Test Method Table 1 Parameters and their levels Symbol Process parameters Unit Level 1 Level 2 Level 3 A Temperature C 80 90 100 B Dye dosage %, o.w.f 2 3 4 C Time min 80 90 100 Table 2 L9 orthogonal array of factors, experimental data, and S/N ratios Experiment number A B C Exhaustion (%) S/N ratio (dB) 1 80 2 80 95.2 39.57 2 80 3 90 94.7 39.52 3 80 4 100 94.3 39.49 4 90 2 90 94.2 39.48 5 90 3 100 93.6 39.42 6 90 4 80 93.1 39.37 7 100 2 100 94.8 39.53 8 100 3 80 93.9 39.45 9 100 4 90 93.8 39.44 123 522 Cellulose (2021) 28:517–532 105-X12. The fastness grades were determined by comparing with the ISO greyscale.

Results and discussion

Determination of optimal conditions

An orthogonal Taguchi technique was applied to determine the best conditions for the highest dye exhaustion percentage. For this, an evaluation of the S/N ratio is a fundamental step in the Taguchi approach. The characteristic quality of the end product was identified by the value of the S/N ratio. The S/N ratio was determined by the deviation values of the characteristics from the desired output. The main purpose of this work was to produce the deepest shade using the D5-based waterless dyeing method. Response outputs are shown in Table 3. The highest mean S/N ratio of each level implies an optimal value for the individual factor. Moreover, these response values were designed with delta statistics values. The delta statistics values were derived from the difference between the highest and lowest average values of each factor of the S/N ratios. Then, the delta characteristics were distributed by ranking methodology, meaning that rank 1 represents the highest value, rank 2 is the second-highest value, rank 3 refers to the third-highest value, and so on. It was evident that the dyebath temperature (A) had the most significant effect with the highest delta (0.10) on the dyeing process, followed by dye dosage (B) (0.09) and dyeing time (C) (0.02).

Furthermore, Fig. 2 shows the corresponding main effect plot of the process parameters for the S/N ratio of the exhaustion percentage. The effectiveness of the individual process parameters was justified by analyzing their values between a horizontal line. In detail, if a specific process parameter is near the horizontal line, that process does not significantly affect the dyeing process. In contrast, a parameter with a higher slope shows the most impact on the dyeing process. Consequently, it was noticed that of the selected factors, temperature and dye mass exhibited a significant effect, while the dyeing time had a relatively small effect on the dyeability. Therefore, the optimum conditions are specified as A1B1C2, which resulted in the maximum exhaustion percentage following the Taguchi approach, because the maximum dye exhaustion indicates the most efficient dyeing performance.

Usually, the exhaustion percentage values increase with an increase in the dyebath temperature. However, in this case, a lower exhaustion value was achieved when the temperature was raised from 80 to 90 °C, but the exhaustion increased with further increasing the dyebath temperature to 100 °C. This decrease was not caused by the degradation of the dye during the dyeing process, that has been proven in Fig. 6. The fiber structure was opened up to a greater extent at higher dyebath temperatures, which facilitates the diffusion of dye molecules into the fibers and achieves maximum exhaustion percentage (El-Shishtawy et al. 2007). Thus, it is likely that most of the dyes were adsorbed into the cotton fiber at 80 °C, and with an increase in temperature, the fiber further swelled, and the absorbed and adsorbed dyes started desorbing into the D5 medium causing a decrease in exhaustion at 90 °C. However, with a further increase in temperature to 100 °C, again the desorbed dye and the leftover dye in the bath started reabsorbing, increasing the exhaustion value. Accordingly, 80 °C was found to be a suitable temperature for optimum exhaustion.

The dye exhaustion percentages improved with increasing dyeing time up to 90 min and then marginally increased at 100 min. Once the dyebath temperature reached 80 C, dye migration also reached equilibrium within 100 min. It was also shown that while the dosage of cacao husk extracts was increased from 2 to 4% o.w.f, a decrease in dye exhaustion percentage of the S/N ratio from 39.53 to 39.44 was observed. However, the dye mass adsorbed into the fiber increased. This implies that there were redundant dyes in the dyebath in the case of 4% o.w.f cacao husk extract dosage.

Interaction plots

An interaction graph is used to understand the interactions between process parameters. Interaction behavior can be defined in two ways: as parallel and non-parallel lines. The occurrence of strong interaction is confirmed through non-parallel lines, and a weak interaction can be described if the lines are parallel (Shafiq et al. 2018). In Fig. 3, factor (A) reveals that there is a strong interaction between the three lines based on its non-parallel nature, while less interaction occurs for factor (B). Also, factor (C) contains a medium interaction plot between their levels. Therefore, this interaction plot indicates that the selected factors had a great influence on the dyeing process.

ANOVA

An assessment of the analysis of variance (ANOVA) provides information about the statistical significance of the optimized model and the contribution percentage of each factor on the dyeing process. Initially, it was designed with a dispersion of characteristic values, sum of squares (SS), and dividing this SS with factors of SS that are carried out in the experimental results. Then, the Fischer’s test value (F-value) was deduced from the ratio of the mean of square (MS) values, which mainly denotes the most influential factor of the model. Very importantly, p values determine whether the factor is significant or not significant related to the experimental designs, and p values less than 0.05 are regarded as significant factors. Table 4 shows the ANOVA performance for the exhaustion percentage. The temperature has a greater influence on E% due to a high F-value of 222.62 and a p value of 0.004 (significant). Secondly, dye mass has shown a medium influence on E% with an F-value of 190.48 with statistical significance (p value of 0.005). On the other hand, the dyeing time had a small effect on E% with an F-value of 7.06 and a statistically insignificant p value of 0.124 ([0.05). Furthermore, the influence of each factor was measured by the contribution percentage (P%). Table 4 shows that the dyebath temperature had the highest contribution percentage at 52.86%, followed by dye dosage of 45.22% of P, and a dyeing time of 1.67% of P.

Residuals plot assessment

The residuals plots for the S/N ratios of exhaustion percentage were investigated and are shown in Fig. 4. The plot is composed of four parts: a normal probability plot, a residuals versus fit, a histogram, and the residuals versus order with respect to the observation number. In general, the normal probability plot approximately follows a straight line, and the obtained plot shows the same trend with most of the points lying on or near the line, so it was confirmed that the residuals are normally distributed during the dyeing process. Second, the residuals versus fit graph demonstrate that lower points are more downwards, while upper points fall randomly near the zero lines, which implies that residuals have a constant variance significance. The histogram bar chart indicates that residuals are normally distributed with a skewness point, which happens when the number of observations order is small. Finally, the residuals versus order have shown that observed residuals are placed randomly around the zero lines, which emphasizes that residuals are dependent on the dyeing process (Sudhakara and Prasanthi 2017).

Fitted plots assessment

The experimental and predicted exhaustion percentages were determined through the fitted plot line graph and are shown in Fig. 5. The graph exhibits good agreement between the predicted and experimental values (R2 = 99.7), and the Pearson correlation coefficient is 0.9974 with a p value of 0.000, indicating that a powerful relationship exists in the dyeing process (Hussain et al. 2010).

Based on the above predictive concept, a regression analysis was initiated to justify the factor's influence on E% and is given as Eq. 5. The equation implies that when the dyeing temperature at 80 C (A1) increases by 1 unit, the E% increases by 0.5556 units. Then, increasing dye mass (2% o.w.f, B1) by 1 unit shows an increase of E% of 0.5556 units, and finally, when the dyeing time increases 90 min (C2), E% increases only by 0.0556 units, which is significantly less than the other two factors. These analyses agree with the optimization and ANOVA results.

$$\begin{aligned} E\% = {} & 94.1778 + \mathbf{0.5556\ A1} - 0.5444\ A2 \\ & - 0.0111\ A3 + \mathbf{0.5556\ B1} - 0.1111\ B2 \\ & - 0.4444\ B3 - 0.1111\ C1 + \mathbf{0.0556\ C2} \\ & + 0.0556\ C3 \end{aligned} \tag{5}$$

Confirmation test

The confirmation test in the Taguchi technique is treated as an essential step to clarify the obtained outputs, and it is highly recommended for statistical analysis. The primary aim of this analysis is to validate the tests and responses. Table 5 presents the results of the confirmation experiments. Once an optimal condition is agreed upon, then the subsequent task is to verify the process optimization. The predicted values were determined using the software. Accordingly, the experiment was performed based on the optimum parameters, and satisfactory improvement in S/N ratio was observed. The exhaustion percentage was improved (increased

S/N ratio of 0.0822) as it was the main purpose of this work. These results demonstrate that systematic statistical experimental design can lead to improved performance.

Dye exhaustion, dye fixation, and colorfastnesses

Natural plant dyes are liable to thermal degradation above 70 C, for example, watermelon extracts(Liman et al. 2020), thus it is critical to test the thermal stability of cacao husk extracts during the exhaust dyeing process because the instability of dyes will influence the calculation of the dye exhaustion percentage (E%) and fixation rate (F%). The thermal stability of cacao husk extracts is shown in Fig. 6. The light absorption values of cacao husk extracts before and after heating at 60–100 C for 100 min were similar, which shows negligible distinctions (0.63–0.66) among the samples. Therefore, it can be concluded that cacao husk extracts in a D5 medium are thermally stable under 100 C in 100 min, i.e. the cacao husk extracts will not degrade during the dyeing process.

For a comparative study, the dyeing performances of the conventional water medium dyeing and D5 medium dyeing process with fixation treatment were evaluated under optimized conditions, and the dye exhaustion (E%), dye fixation (F%), and total fixation (T%) values are shown in Table 6. The E% value for the conventional dyed sample was nearly half of the D5 dyed sample. The cotton fiber was dry and hydrophilic; when the fiber was immersed in the D5 dyebath, the little water content of dye solution evenly dispersed in the D5 medium was quickly absorbed into the fiber, accompanied with adsorption of dyes onto the fiber because the dye was in a soluble state in water. After adsorption, the ‘‘water pool’’ was damaged. Besides, D5 repels water due to its hydrophobic property; thus, the adsorption processes were irreversible. During the rotating dyeing process, the dye solution in D5 medium without dye aggregation (Wang et al. 2016) was continuously transferred from the D5 dye bath to the fiber, resulting in higher dye exhaustion compared to the conventional medium dyeing. Of course, a small quantity of dye solution possibly desorbed if the ‘‘water pool’’ was not broken; meanwhile, the surfactants and co-surfactants adsorbed on the surface of the fiber also possibly contributed to impeding the dye solution adsorption. Therefore, the dye solution was not completely absorbed into the fiber, i.e., 100% dye exhaustion.

Without a fixation treatment, the F% of the conventional dyed cotton fabric and the D5 dyed cotton fabric were 20.4% and 45.3% respectively, and their T% values were 9.8% with a K/S of 2.0 and 43.3% with a K/S of 8.1. The main composition of cacao husk extracts includes catechin, epicatechin, and procyanidin B2 (Okiyama et al. 2018), whose structures can be expressed as compound (b) in Fig. 7. In the exhaust dyeing process, the cacao husk extracts were physically adsorbed in the cotton fiber (compound (d) in Fig. 7) possibly by H-bonds and Van der Waals forces between the fiber and dyes, and between the dyes and dyes. Thus, after soaping, mainly the adsorbed dyes were washed off.

With a fixation treatment, the fabrics dyed in water medium were treated by the fixation treatment in a water medium and a D5 medium, and the F% values were 35.3% and 90.5% and the T% values were 17.0% and 43.6%, respectively. Besides, in the case of the fabric dyed in the D5 medium, the F% values were 62.4% and 94.8% for the dye fixation treatment in water and in the D5 medium, respectively, and their T% values were 59.7% and 90.6%, respectively. The fixation treatment was effective in improving the dye fixation values. This implies that the cationic fixation agent performed well in fixing the cacao husk extracts, especially in the D5 medium fixation treatment. The main composition of the cationic dye-fixing agent is polyethylenepolyamine, whose structure was expressed as compound (c) in Fig. 7. After the fixation treatment, the cationic polyethylenepolyamine acted as a cross-linking agent to form ionic bonds between the cacao husk extracts and fibers in the hydroxyl groups (compound (f) in Fig. 7). Meanwhile, since the cationic dye-fixing agent is a polymer, it formed a membrane on the surface of the dyed fiber, which also contributed to fixing the dyes in the fiber. The dyes fixed by the dye-fixing agent were stable and persisted in the fiber after soaping, while the unfixed dyes were washed off after the soaping process, and this reaction scheme is shown in Fig. 7. The F% increment by the fixation treatment in the D5 medium is higher by about 30% than the same treatment in the water medium, in which it was possible that a high amount of the cationic dye-fixing agent was absorbed in the dyed fiber in the D5 medium in contrast with that in the water medium. Furthermore, the considerable promotion of dye fixation by the treatment in D5 was characterized by the color strength of the dyed fabric, which was about 4–5 values higher than the same treatment in water. The highest K/S value was 15.6, which appeared in both the dyeing and dye fixation treatments in the D5 medium.

After the fixation treatment, the colorfastness to washing and rubbing of the cotton fabric was improved, which are listed in Table 7. These results can be further correlated with their photographic images, as shown in Fig. 8. In the conventional water medium dyeing, the color shade of the dyed cotton fabric without fixation treatment showed obvious changes to light after soaping. In contrast, the color shade of the dyed cotton fabric in the D5 medium with fixation treatment in the D5 medium was resistant to soaping as the colorfastness grades were particularly good. The performance data shows that dyeing and fixation of cotton fabric in the D5 medium are feasible.

Conclusions

In this work, we demonstrated that the waterless micellar dyeing of cotton fabric with cacao husk extracts can be carried out in D5 medium, which is an eco-friendly dyeing process, as the spent D5 dyebath can be recycled and reused without producing any effluent. A series of experiments were conducted following the Taguchi experimental design, and optimal conditions of 80 C temperature, 2% o.w.f Table 7 Colorfastness properties Water medium dyeing D5 medium dyeing Without fixation treatment Wash fastness 2 3 Rubbing fastness Dry (grade) 4 3–4 Wet (grade) 3 3 With fixation treatment Wash fastness In water 2–3 3–4 In D5 4 4 Rubbing fastness Dry (grade) In water 4 4 In D5 5 5 Wet (grade) In water 3–4 4 In D5 4 4 Fig. 8 Photographic images of dyed fabric, a conventional water medium dyeing without fixation treatment, before soaping, b conventional water medium dyeing, without fixation treatment, after soaping, c D5 medium dyeing with a D5 fixation treatment, before soaping, and d D5 medium dyeing with a D5 fixation treatment, after soaping 123 530 Cellulose (2021) 28:517–532 of cacao husk extracts, and a dyeing time of 90 min were obtained. Two significant factors—temperature and dye mass—were determined through ANOVA analysis for the dyeing process. The fitted plot assessment indicated a good fit model with an R2 value of 99.7. Then, the validation of the obtained results was tested, and the value of the S/N ratio was improved to 0.0822. The exhaustion level (95.6%) of cacao husk extract dye using the D5-based waterless dyeing method was considerably higher than the exhaustion level (48.2%) achieved for the conventional aqueous dyeing method. The dyed cotton by the D5 medium dyeing was treated with a cationic dyefixing agent in a D5 medium and showed a high fixation rate of 94.8% and a total fixation percentage of 90.6%. Also, a deep shade of dyed cotton fabric was achieved with a K/S value of 15.6. The colorfastness to washing and rubbing were satisfactory. This novel method could also be used for the dyeing of cotton fabric with other natural dyes.

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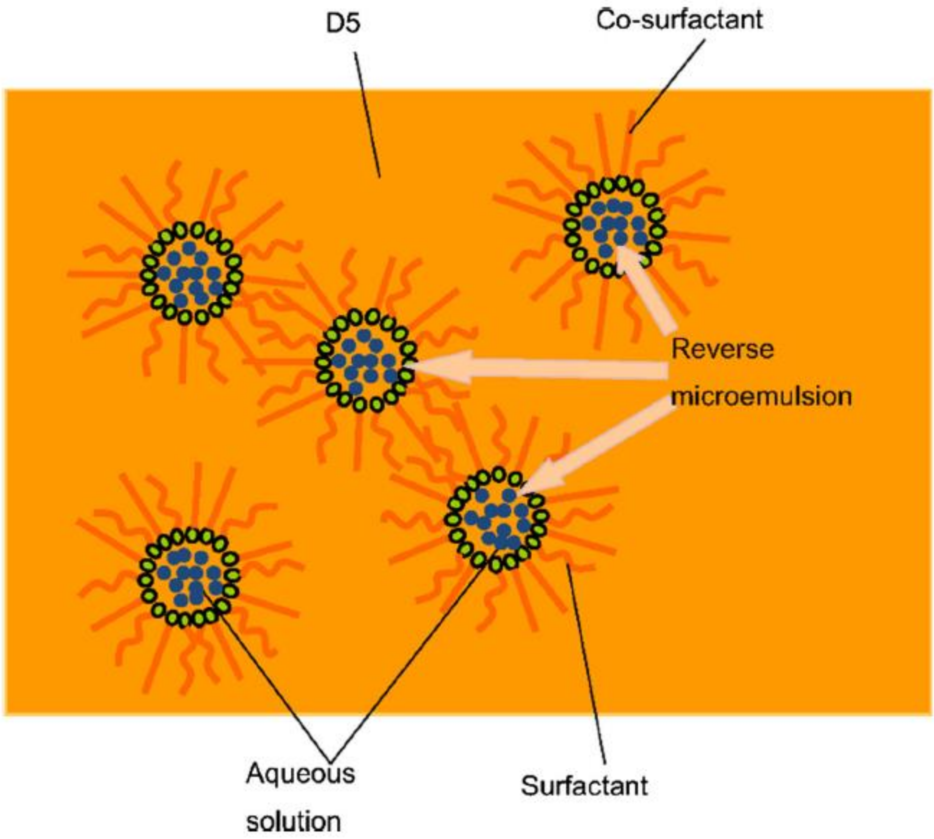

Fig. 1 Schematic diagram of microemulsion in D5 medium (Pei et al. 2017)

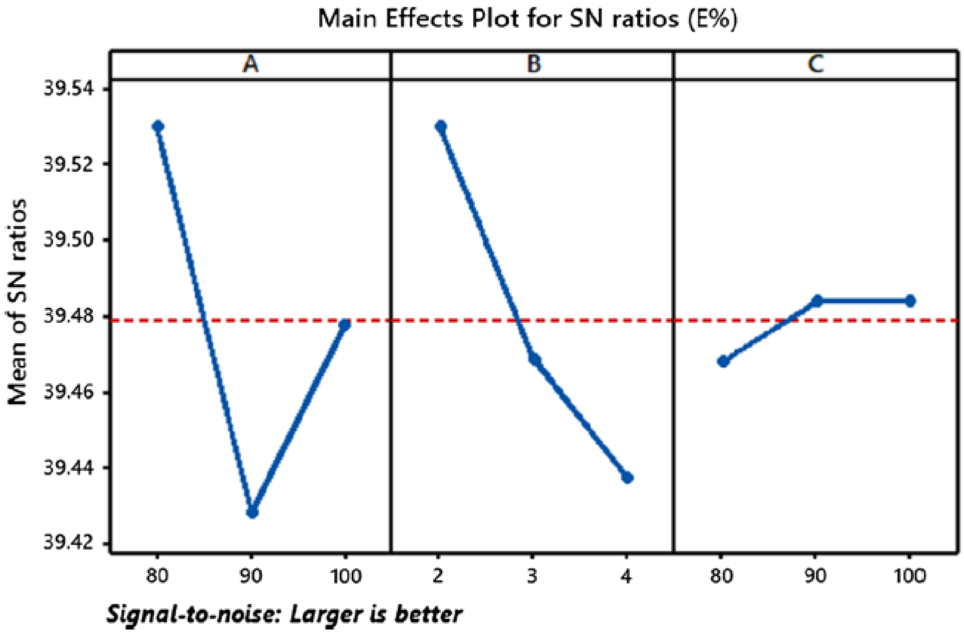

Fig. 2 Main effect plot for S/N ratio of exhaustion percentage (E%)

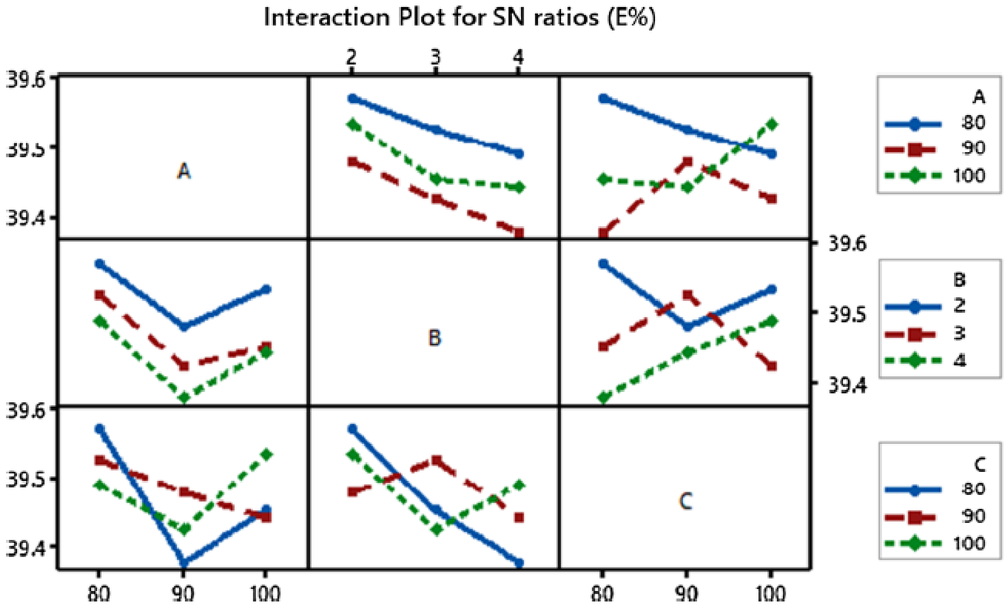

Fig. 3 Interaction effect plot for S/N ratio of exhaustion percentage (E%)

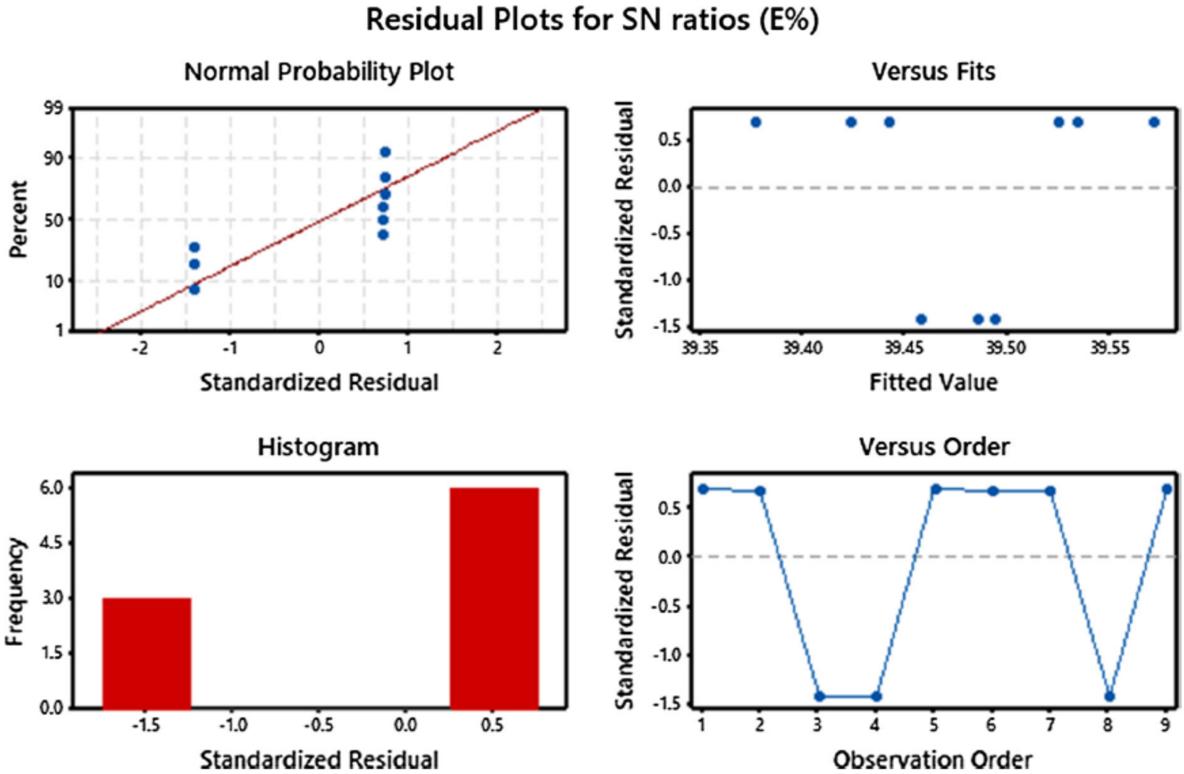

Fig. 4 Residual plots for the S/N ratios of E%

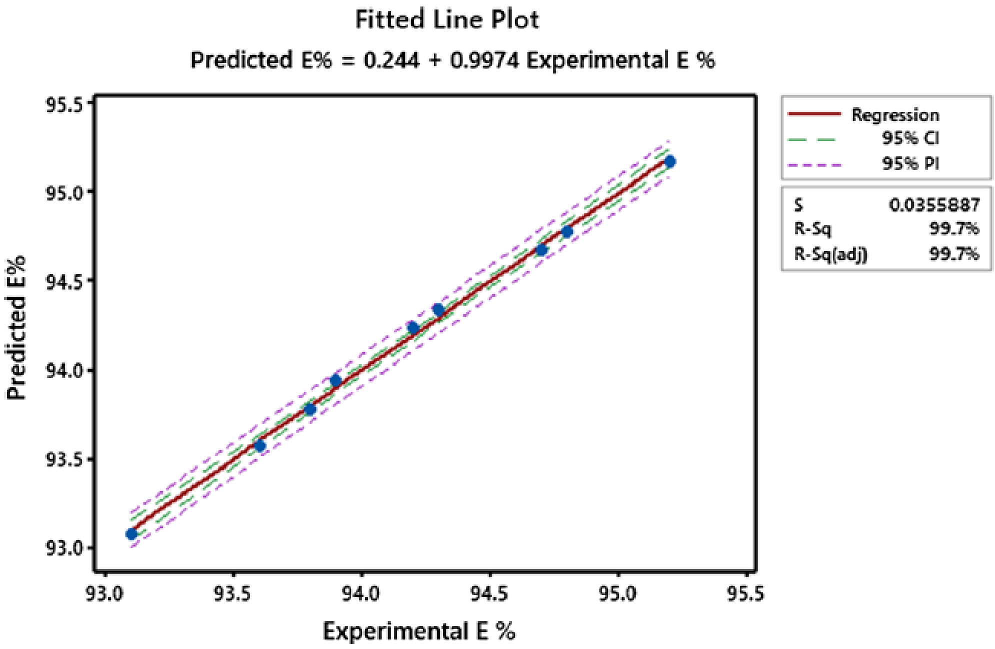

Fig. 5 The fitted line for the experimental and predicted exhaustion E%

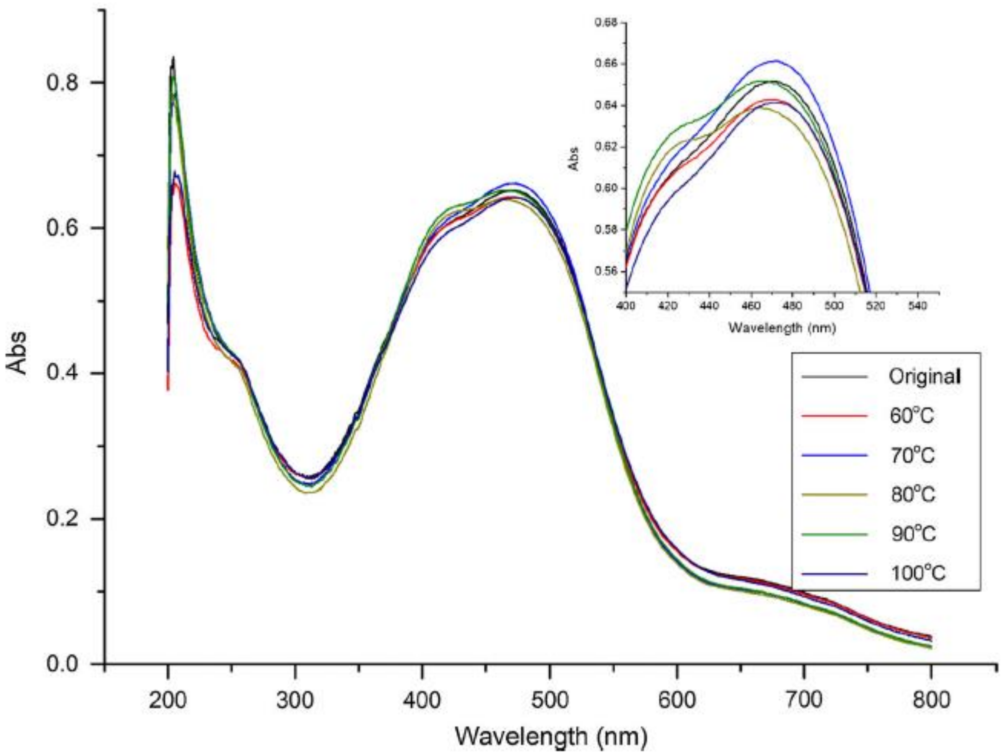

Fig. 6 Thermal stability of cacao husk extracts in a D5 microemulsion

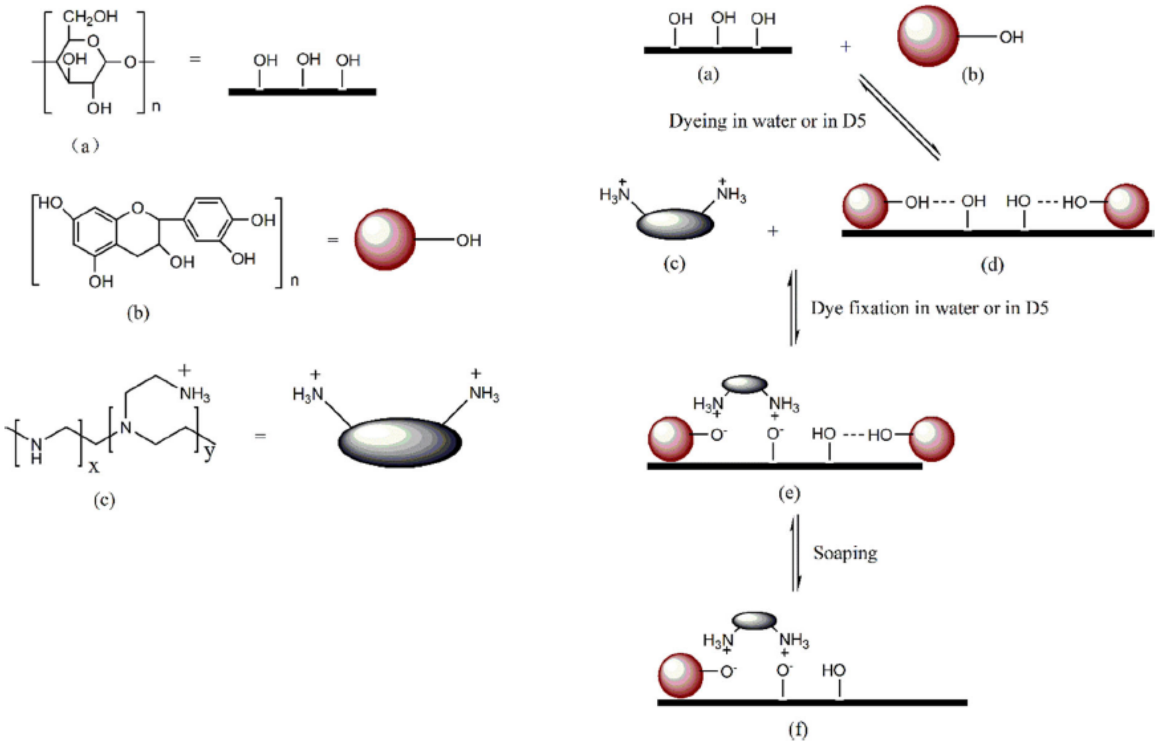

Fig. 7 Reaction scheme of dyeing cotton fabric with cacao husk extracts in a water medium and a D5 medium, and a fixation treatment with a cationic fixing agent in a water medium and a D5 medium

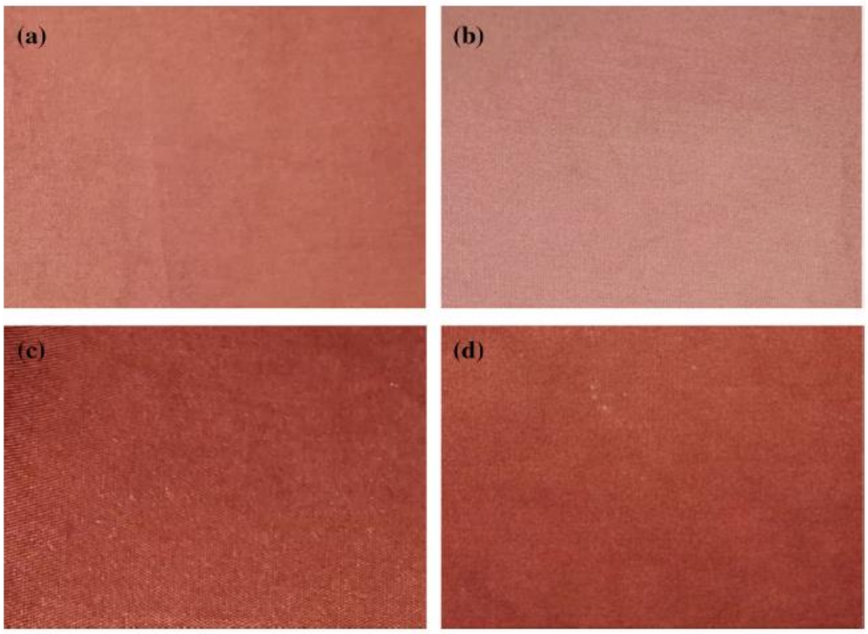

Fig. 8 Photographic images of dyed fabric, **a** conventional water medium dyeing without fixation treatment, before soaping, **b** conventional water medium dyeing, without fixation treatment, after soaping, **c** D5 medium dyeing with a D5 fixation treatment, before soaping, and **d** D5 medium dyeing with a D5 fixation treatment, after soaping

Table 1 Parameters and their levels

Symbol	Process parameters	Unit	Level 1	Level 2	Level 3
A	Temperature	°C	80	90	100
B	Dye dosage	%, o.w.f	2	3	4
C	Time	min	80	90	100

Table 2 L^9 orthogonal array of factors, experimental data, and S/N ratios

Experiment number	A	B	C	Exhaustion (%)	S/N ratio (dB)
1	80	2	80	95.2	39.57
2	80	3	90	94.7	39.52
3	80	4	100	94.3	39.49
4	90	2	90	94.2	39.48
5	90	3	100	93.6	39.42
6	90	4	80	93.1	39.37
7	100	2	100	94.8	39.53
8	100	3	80	93.9	39.45
9	100	4	90	93.8	39.44

Table 3 Response table for S/N ratios (E%)

Level	A	B	C
1	39.53	39.53	39.47
2	39.43	39.47	39.48
3	39.48	39.44	39.48
Delta	0.10	0.09	0.01
Rank	1	2	3

Table 4 ANOVA for the S/N ratio (E%)

Source	DF	SS	MS	F	*p* value	Remarks	P (%)
A	2	0.015452	0.007726	222.62	0.004	Significant	52.86
B	2	0.013221	0.006610	190.48	0.005	Significant	45.22
C	2	0.000490	0.000245	7.06	0.124	Not significant	1.67
Residual error	2	0.000069	0.000035				0.23
Total	8	0.029231					

Table 5 Results of the confirmation experiment

Level	Initial parameters A1B2C3	Prediction A1B1C2	Confirmation experiment A1B1C2
E%	94.7	95.3	95.6
S/N	39.5270	39.5864	39.6092
Improvement in S/N ratio		0.0822	

Table 6 Dye exhaustion, dye fixation, and color strength

	Water medium dyeing	D5 medium dyeing
Exhaustion (%)	48.2	95.6
Without fixation treatment		
Fixation (%)	20.4	45.3
Total fixation (%)	9.8	43.3
K/S	2.0	8.1
With fixation treatment		
Fixation (%)		
In water	35.3	62.4
In D5	90.5	94.8
Total fixation (%)		
In water	17.0	59.7
In D5	43.6	90.6
K/S		
In water	3.9	11.3
In D5	9.4	15.6

Table 7 Colorfastness properties

	Water medium dyeing	D5 medium dyeing
Without fixation treatment		
Wash fastness	2	3
Rubbing fastness		
Dry (grade)	4	3–4
Wet (grade)	3	3
With fixation treatment		
Wash fastness		
In water	2–3	3–4
In D5	4	4
Rubbing fastness		
Dry (grade)		
In water	4	4
In D5	5	5
Wet (grade)		
In water	3–4	4
In D5	4	4