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Statistical optimization and bulk scale validation of the effects of cationic pre-treatment of cotton fabric for digital printing with reactive dyes

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Abstract

Digital printing has the potential of enabling cleaner printing or even dyeing of cotton fabrics (Lin and He 2018). However, whilst effluent-free digital printing and dyeing of synthetic textile fabrics have seen some success (Alchemie Technology 2020), the same remain elusive for cotton fabrics. The study reported in this paper aimed to optimize the process parameters of cationic pre-treatment with a view to creating a cleaner cotton fabric digital printing process that could be sustainably implemented at bulk-scale production. Thus, process variables were screened using the one-factor-at-a-time approach to select optimum experimental regions. A Box–Behnken design was used to investigate the combined effect of selected factors namely amount of thickener (150−200 g/L), urea (75−125 g/L) and alkali (10–20 g/L) on the color strength, dye fixation and ink penetration of cationized and digital-printed cotton fabrics. The significant models showed excellent fitting of the data. The optimum levels of the factors namely amount of thickener, urea and alkali were found 200 g/L, 125 g/L and 10 g/L, respectively. The bulk scale experiments carried out at optimum levels have shown that an average of ca. 52% of reactive ink, 37.5% of urea and

50% of alkali can be saved by digital printing of cationized cotton along with generation of nearly colorless effluent.

Keywords: Cotton; Cationization; Digital Printing; One-factor-at-a-time; Box–Behnken design; Optimization

Introduction

Arguably the most infamous aspect of the textile coloration industry has been fresh water consumption and creation of a proportionally large volume of effluent that is a cocktail of chemicals. The magnitude of this problem is notably different for different wet processes, however, generally all wet processes are of great concern when it comes to handling of the process effluent (Schramm and Jantschgi 1999, Kalliala and Talvenmaa 2000). Therefore, to address such issues, ambitious programs were undertaken by academia and industry and detailed accounts of such momentous efforts are available in literature (O'Neill, Hawkes et al. 1999, Khatri, Peerzada et al. 2015). Both in academic and industrial research of relevance, focus has been on a multitude of aspects; from improved molecular structures of dyestuffs to radically new classes of colorants and from highly efficient machine designs to new process routes and so on (Lewis 1999, Hashem 2006, Ahmed and El-Shishtawy 2010, Fu, Hinks et al. 2013, Lei, Gong et al. 2013, Ali, Khatri et al. 2014, Ali, Mughal et al. 2015). As far as the coloration of cotton (and other fibers also) is concerned, one major research theme that has drawn considerable attention of researchers all over the world is the maximization of the transfer and/or retention of colorant onto the substrate surface while limiting the consumption of the chemicals and auxiliaries involved (Hauser and Tabba 2001, Wang and Lewis 2002, Burkinshaw and Kabambe 2011, Shu, Fang et al. 2018).

One of the most sought-after techniques to achieve the aforementioned objectives is surface and/or bulk modification of cotton fiber which can be brought about by physical

methods such as plasma treatment (V D Gotmare, Kartick K Samanta et al. 2015, Zille, Oliveira et al. 2015). Modification of cellulosic fibers aimed at improved colorant-substrate interaction can also be achieved by treatment with a range of chemical compounds (Patiño, Canal et al. 2011, Mahbubul Bashar and Khan 2013, Das, Bakshi et al. 2014). The two techniques, i.e., physical treatments and chemical treatments can be employed in conjunction to each other (Ristić, Jovančić et al. 2010, A G Demir, F R Oliveira et al. 2018). It is noteworthy that there are no explicit reports of the physical modification techniques to be better (in terms of the characteristics of the end product) than the chemical techniques or vice versa and there are numerous studies reporting the pros and cons of both techniques for conventional dyeing and printing (Montazer, Malek et al. 2007, Wang and Zhang 2007, Wang, Ma et al. 2009, Samanta, Kar et al. 2016) and for the rapidly growing inkjet printing also (Kan, Yuen et al. 2011, Park and Koo 2014, Pransilp, Pruettiphap et al. 2016).

Cationic treatment of cotton is arguably one of the most well researched among the various chemical modification techniques for cotton (Samanta, Kar et al. 2015, Wolela 2019, Correia, Rainert et al. 2020). Cationic agents impart a positive charge on the surface of fibers (cellulose) thus improving the interaction between anionic dye stuffs, for instance reactive dyes, and the substrate (El-Shishtawy and Nassar 2002, Ristic and Ristic 2012). The present study pertains to cationization of cotton using 3-chloro-2-hydroxypropyl trimethylammonium chloride for improved dye-fiber interaction thus resulting in reduced consumption of dye and auxiliary chemicals (or improved dye fixation in reactive inkjet printing). It is well established that in the presence of alkali, 3-chloro-2 hydroxypropyl trimethylammonium chloride (CHPTAC) is converted to 2,3-epoxypropyltrimethylammonium chloride (EPTAC) together with partial dissociation of the cellulose hydroxyl group. The produced EPTAC reacts with the primary hydroxyl

group of ionized cellulose under alkaline conditions to form the cationized cotton fiber (Arivithamani and Giri Dev 2017, Correia, Rainert et al. 2020).

Previous studies show that colour yield in reactive inkjet printing is considerably higher on cationized cellulosic fibers (Rekaby, Thalouth et al. 2013). This is often accompanied with reduced consumption of auxiliary chemicals and shortening of steaming time (Kanik and Hauser 2002). It is also reported that besides the aforementioned advantages, cationization also results in improved quality of ink-jetted images (Yang, Fang et al. 2019). Attempts have been made by researchers to devise a single step process to achieve obvious advantages (Ma, Shen et al. 2017). Despite some promising results, there are issues such as competition between reactive dye and CHPTAC in large scale application (Wang, Hu et al. 2018). Thus, interaction between the cationizing agent and other auxiliary chemicals is also important to be considered as this can have a marked effect on the inkjet printed product characteristics (Chen, Zhao et al. 2004, Yuen, Ku et al. 2007). Design of Experiments (DoE) can be effectively employed to analyse the interaction between a large number of 'factors' that can potentially influence inkjet printing (Faisal and Tronci 2018, Faisal, Tronci et al. 2019). To the best of our knowledge, a detailed statistical account of various influencing factors on inkjet printing along with a consideration of the effect of cationization is not available. Therefore, in the present study, one-factor-at-a-time approach for screening followed by Response Surface Methodology (RSM) was employed to optimize the printing properties of the cationized digital-printed cotton. Later, the process was scaled up to bulk scale for validation of lab scale results. Importantly, the extent of improvement on cleanness of production, in terms of reduction in residual dyes in the wash-off liquor, was also studied.

Experimental

Material

CR-2000 (3-chloro-2-hydroxytrimethyl propyl ammonium chloride, Dow, UK) was kindly supplied by iTextiles Pakistan. Diamontex HD-CN (polyacrylicamide, thickener Diamontex, Italy), Revatol S (Sodium metabisulphite, mild oxidizing agent, Archroma), Ladipur RSK (Archroma) were supplied by StyleTex Pakistan Limited. Sodium hydroxide (NaOH), acetic acid, urea (humectant) and sodium bicarbonate (alkali) were purchased from local market and were of laboratory grade. BEZAJET Magenta R (monochloro-s-triazine, CI Reactive Red 218, Bezema Colour Solutions) reactive ink and ready-to-print cotton fabric [Plain weave (1/1); 130 g/cm^2, 60-inch width] were generously supplied by Gulahmed Textile Mills (Pakistan).

Methods

Cationization of Cotton fabric

Cationization of the substrate was carried out using previously reported cold pad–batch method (Hashem 2006). The experimental procedure adopted was as follows: CHPTAC (25, 50, 75, 100 and 125 g/L) was dissolved in water and then appropriate amount of NaOH (32, 40, 47, 55 and 63 g/L) was added into the solution. Cotton fabric of 20 × 30 cm was then padded to a wet pick-up of 100%, and then batched overnight in a plastic bag at room temperature. After cationization, each fabric sample was rinsed with cold water (temperature between 20 and 22 °C) containing acetic acid (1% w/w) for 5 minutes. After the neutralization, samples were washed using tap water for 10 minutes. The samples were dried in ambient conditions for 24 hours.

Pretreatment of Cationized Cotton

In order to prepare the padding liquor, appropriate amounts of urea, alkali, thickener and 15 g/L of mild oxidizing agent were used. The liquor was then made up to 1000 mL with deionized water. For proper homogenization of the padding liquor, the mixture was stirred at room temperature for 15 minutes. The cationized cotton fabric samples were padded with the pretreatment liquor to achieve a pick-up of 80-90%. For this, the padder pressure was maintained at 2.2 bar while the padding speed was 2.0 RPM. Prior to digital printing, the pre-treated (padded) fabric substrates were dried in an oven at 100 °C for 2 minutes and then conditioned. The untreated (un-cationized) cotton fabric samples were also pre-treated in exactly the same manner as described in the preceding text.

Digital Printing of Cationized Cotton

Digital printing of the samples was carried out on MS JP7 evo printer. This printer is equipped with Kyocera piezo drop-on-demand print head. The cationized fabric samples were printed at 600×600 dpi as a solid rectangular pattern (5×12 cm). After printing, the fabric samples were air dried for 5 minutes and fixation of the print was carried out using saturated steam at 102 °C for 10 minutes. Subsequently, washing-off of the printed fabric samples was carried out according to the method previously reported by authors (Faisal, Tronci et al. 2019). Lastly, the samples were dried at ambient temperature for 24 hours.

One Factor at a Time

Previously established essential factors including the amounts of CHPTAC, alkali, urea and thickener were screened using one-factor-at-time for digital printing of cotton fabric (Kanik and Hauser 2002, Kaimouz, Wardman et al. 2010, Rekaby, Thalouth et al. 2013, Faisal and Tronci 2018, Faisal, Tronci et al. 2019, Correia, Rainert et al. 2020). On the

basis of this study, the factors which had significant effect on color strength (K/S) and fixation (F%) values were chosen for the response surface methodology (RSM) study. The conditions for one-factor at a time were set based on author's previous work (Faisal 2019) and detailed as follows: amount of CHPTAC (25, 50, 75, 100 and 125 g/L), amount of alkali (0, 5, 10, 15, 20 g/L), amount of urea (75, 100, 125, 150, 175 and 200 g/L) and amount of thickener (100, 125, 150, 175 and 200 g/L). All experiments were done in triplicates and results were expressed as average.

The data pertaining to the screening of factors using OFAT is shown in Figure S1, provided as supplemental material. It was observed that all four factors show a significant effect on colour strength (K/S), dye fixation (F%) and ink penetration (P%) of cationized and digitally printed cotton. However, increase in amount of CHPTAC beyond 75 g/L does not have significant effect on printing properties. Hence, for RSM optimization studies, amount of CHPTAC was chosen constant as 75 g/L.

Box-Behnken Design and statistical analysis

After screening and preliminary estimation of the range of process variables, the amount of thickener, the amount of urea, and the amount of alkali were defined as the three factors for Box–Behnken design (BBD). The coded and uncoded values of the experimental design factors are listed in Table 1. Each selected factor has three levels: the amount of thickener (150, 175 and 200 g/L), the amount of urea (75, 100 and 125 g/L), and the amount of alkali (10, 15 and 20 g/L). The K/S, F% and P% of the cationized and digital-printed cotton fabric were defined as the responses or dependent variables. The complete BBD design consists of 12 experimental points and 3 centre points and is shown in Table 2. All experiments were carried out in a random order.

In response surface methodology, a polynomial response surface is used to depict the relationship between predicting variables X and a response Y. The generalized functional relationship for a quadratic model with three factors is defined in Equation (1):

$$Y_0 = \alpha_0 + \sum_{i=1}^{3} \alpha_i X_i + \sum_{i=1}^{3} \alpha_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=1} \alpha_{ij} X_i X_j \quad (1)$$

In Equation 1, X_i and X_j represent the experimental factors. Accordingly, Y_0 represents the response, α_o is the intercept, α_i, is the regression coefficient of the linear terms, α_{ii} is the regression coefficient of the quadratic terms, and α_{ij} are the regression coefficient of the interactive terms.

The regression coefficients were determined according to the Analysis of Variance (ANOVA) method. The regression coefficients were then used to generate response surface plots and contour plots from the regression model. A p-value of less than 0.05 was considered to be statistically significant. Minitab 17 software was used to analyze the experimental data.

Insert Table 1 here

Validation at bulk Scale

For validation of optimized parameters, the 20 m of cotton fabric was cationized and digital-printed at bulk scale. For comparison, 20 m of cotton fabric was also digital printed by conventional digital method.

Characterization of Cationized Cotton prepared at bulk scale

Nitrogen content (N%) of untreated and cationized cotton was determined by the Kjeldahl method previously reported in literature. Morphological features of untreated and cationized cotton fabric were studied by using Philips® XL 30 Scanning Electron

Microscope. X-ray diffraction of untreated and cationized cotton fabric was carried out by using PANalyticalX'pert pro X-ray diffractometer using Cu-Kα radiation of wavelength λ = 0.1541 nm.

Printing Properties of Cationized and Digital-Printed Cotton prepared at bulk scale

The assessment of cationized and digital-printed cotton fabric was done on Datacolor Spectrophotometer (D65). The reflectance values (R) of samples were taken before and after washing according to the procedure described previously. The K/S, F% and P% of cationized and digital-printed cotton fabric were calculated using Equations 2, 3 and 4, respectively.

$$K/S = \frac{(1-R)^2}{2R} \tag{2}$$

$$F\% = \frac{(K/S)_{before\ wash}}{(K/S)_{after\ wash}} \times 100 \tag{3}$$

$$P\% = \frac{100(K/S)_{back}}{0.5[(K/S)_{front} + (K/S)_{back}]} \tag{4}$$

Fastness Properties of Cationized and Digital-Printed Cotton

Fastness properties including wash fastness and crock fastness tests of untreated and cationized and digital-printed cotton fabric were carried out according to BS EN ISO 105 C06/E2S (British Standards Institution 2010) and AATCC TM08 (The American Association of Textile Chemists & Colorists 2016).

Results and Discussion

RSM Optimization

Model Fitting

For response surface methodology based on the BBD, 15 experimental runs with different combinations of three factors namely amount of thickener (X1), amount of urea (X2) and amount of alkali (X3) were carried out and the results are shown in Table S1 (supplemental Material). The obtained models were reduced by using forward selection regression. Adequacy of the regression models was statistically evaluated by ANOVA, coefficient of determination (R^2), F-test, lack-of-fit and p-values for the model and the results are given in Table S2 (supplemental Material). The terms with p-values less than 0.05 are statistically significant at 95% confidence level. The final response surface equations for K/S, F% and P% are given in Equations 5, 6 and 7 respectively.

$$K/S = 8.501 + 2.168X1 - 0.282X2 + 0.558X3 + 1.472X1^2 + 0.488X3^2 - 0.548X2X3 \quad (5)$$

$$F\% = 88.504 + 5.312X1 + 1.209X2 - 0.975X3 \quad (6)$$

$$P\% = 36.289 - 4.162X1 + 5.098X2 - 0.373X3 - 2.062X2X3 \quad (7)$$

It is evident from Table S2 that all the three factors, namely amount of thickener (X1), amount of urea (X2) and amount of alkali (X3) have significant effect on both K/S and F% values of cationized and digital-printed cotton. However, amount of thickener and amount of urea have significant effect on P%. As far as the interaction effects are concerned, only interaction between amount of urea and amount of alkali (X2X3) has significant effect on both K/S and P%. Among the quadratic terms, the quadratic effect of amount of thickener ($X1^2$) and amount of alkali ($X3^2$) are found to be statistically significant for K/S. From Table S2, it is observed that the R^2 for K/S, F% and P% are

0.99, 0.96 and 0.95, respectively. Higher R2 values imply a good fit of response surface equation to the experimental data. Table S2 also demonstrates that the lack-of-fit p-values of the models are insignificant. The models are deemed adequate for the prediction within the range of experimental variables examined.

The response surface equations for K/S, F% and P% are given in Equations 5-7 respectively. From Equation 5, it can be seen that the positive coefficients of X1, X3, $X1^2$ and $X3^2$ indicated contributions that may increase K/S, while the negative coefficients of X2 and X2X3 indicated an unfavorable effect on K/S of cationized and digital-printed cotton. In addition, the coefficients of X1 and X2 have positive and the coefficient of the X3 has negative effect on F% (Equation 6) of cationized and digital-printed cotton. Whilst for P% (Equation 7) X2 has positive while X1 and X3 and X2X3 have negative effect.

3D surface plots were constructed based on the reduced model equations and are shown in Figure 1. It is evident from Figure 1(a–c) that K/S increases with increasing amount of thickener and alkali and with decreasing amount of urea. However, the effect of amount of thickener on the increase in K/S is greater than that of amount of urea and alkali. It can be further seen that there is a significant negative interaction between amount of urea and amount of alkali (X2X3). It is evident from Figure 1(d–f) that an increase in amount of thickener and urea and decrease in the amount of alkali results in an increase in the F% of the cationized digital-printed cotton. Once again, the effect of amount of thickener is more pronounced than that of other factors. It is apparent from Figure 1(g–i) that P% of cationized digital-printed cotton fabric increases with increasing amount of urea and decreases with increasing amount of thickener and alkali. It can be further seen that there is a significant negative interaction between amount of urea and amount of alkali (X2X3).

Insert Figure 1 here

Optimization and Validation

All the responses were concurrently optimized by multi-response analysis by using Derringer's desirability function methodology. The desired responses were to maximize and same importance was assumed for each response. Applying the methodology, the optimum levels of the factors were found 200 g/L of thickener (X1), 125 g/L of urea (X2) and 10 g/L of alkali (X3) with the corresponding desirability (D) value of 0.814 (Figure S2). The optimal amount of urea and amount of alkali were much lower than those previously reported values of 200 g/L of urea and 20 g/L of alkali (Faisal 2019) thus also contributing to the sustainability of the proposed process. These factor level combinations predicted the responses K/S of 12.34, F% of 96% and P% of 39.66%.

To validate the optimal parameters and predicted responses calculated, confirmatory experiments were conducted at Gulahmed Textile Mills Limited using the optimized parameters at bulk scale. The results are listed in Table 2 and were found closely co-related with the data obtained from optimization analysis using Derringer's desirability function.

Characterization of Cationized Cotton prepared at bulk scale

The nitrogen content (N %) of the cotton fabric cationized with 75 g/L of CHPTAC was found to be 0.59%.

The SEM images of untreated and cationized cotton samples have been illustrated in Figure S3 (supplemental material). From Figure S3(b), it can be seen that the surface of the cationized fibres becomes a little rougher as compared to untreated fibres [Figure S3(a)]. Such an increase in roughness can be related to the deposition of the CHPTAC onto the surface of the fibres (Khalil-Abad, Yazdanshenas et al. 2009).

The XRD spectra of untreated and cationized cotton samples are shown in Figure S4 (supplemental material). It can be seen that representative diffraction peaks of cotton existed at 2θ of 14.3°, 16.3°, 22.2°, 33.8° and 44.6° for both untreated cotton and cationized cotton. These peaks correspond precisely to cellulose I crystalline form of cotton. The results of XRD spectra reveal that the crystalline form in cotton has not been changed due to cationization process.

Printing Properties of cationized and digital-printed Cotton prepared at bulk scale

The printing properties of the untreated and cationized cotton pretreated with 200 g/L of thickener, 125 g/L of urea, 10 g/L of alkali and 15 g/L Revatol S and then digital printed with magenta reactive ink are summarized in Table 2. It can be seen from Table 2 that the K/S and F% values increase drastically for cationized cotton using less amount of urea and alkali as compared to the untreated and digital-printed cotton. The experiments carried out in the present study have shown that an average of ca. 52% of reactive ink, 37.5% of urea and 50% of alkali can be saved by digital printing of cationized cotton as compared to digital printing of untreated cotton, owing to nearly 96% fixation of the applied ink. These results indicated that with the cationized and digital-printed cotton under the optimized conditions, improved K/S and F% along with acceptable P% can be achieved by consuming reduced amount ink, urea and alkali. In addition, it can also be seen from Table 2 that uniform and bright color print was obtained at mini-bulk scale using the optimum process parameters.

Insert Table 2 here

Fastness Properties and tear strength of cationized and digital-printed Cotton

The color fastness properties and tear strength of the untreated and cationized cotton are

summarized in Table 2. It can be seen from Table 2 that the wash fastness and dry crock fastness are comparable to the results of untreated cotton whereas wet crock fastness of cationized samples slight deteriorated. This could be the result of the higher dye concentration and low penetration i.e. higher surface coloration on the cationized cotton (Kanik and Hauser 2004). It can also be seen that the tear strength of cationized and digital-printed cotton was not affected significantly as compared to untreated cotton.

Environmental Impact

Figure 2 shows UV/Vis spectroscopic results and digital image of the washing-off liquors for the untreated and cationized and digital–printed cotton. From Figure 2, it can be seen that UV/Vis absorbance of the washing-off liquor of the cationized and digital-printing fabric is significantly lower as compared to that of the untreated and digital printing fabric. In addition, it is clear that nearly colorless effluent was obtained by digital printing of cationized cotton fabric demonstrating that markedly less dye was released in the effluent compared to traditional digital printing method. Therefore, the proposed process has good potential for providing more environment friendly printing method using less amount of pretreatment chemicals and reactive ink and generating nearly colorless effluent.

Insert Figure 2 here

Economic Analysis

Cost analysis of the cationic pre-treatment of cotton and digital printing that was optimised in the present study is provided in Table S3 (Supplementary Material). The per unit cost of dye and auxiliaries that is considered is obtained from the industry where the bulk scale trials were carried out. Similarly, the cost of the cationic pre-treatment is obtained from the concerned industry and includes the cost of padding, washing and

subsequently drying on stenter. This analysis is based on a consideration of only the amount of reactive dye that is wasted as a result of hydrolysis during printing of the selected substrate. The calculations provided in Table S3 reveal that that the proposed cationic pre-treatment of cotton prior to digital printing results in savings of Rs 235148 (USD 1495) per day while maintaining comparable fastness properties.

Conclusions

A bulk scale process for digital printing of cationized cotton was successfully designed. The digital printing of cationized cotton fabric showed that the uniform and bright color print was obtained at bulk scale using optimum process parameters. Moreover, the cationically treated and digital-printed cotton fabric also presented excellent color fastness to washing and crocking, rated at 4, 5 (Dry) and 4 (Wet), respectively. In addition, printing of cationized cotton at bulk scale demonstrated significant environmental advantages of the cotton fabric printing method that combines cationization and digital printing, in terms of reduced consumption of reactive ink and pretreatment chemicals (urea and alkali) whilst, very importantly, generating nearly colorless effluent.

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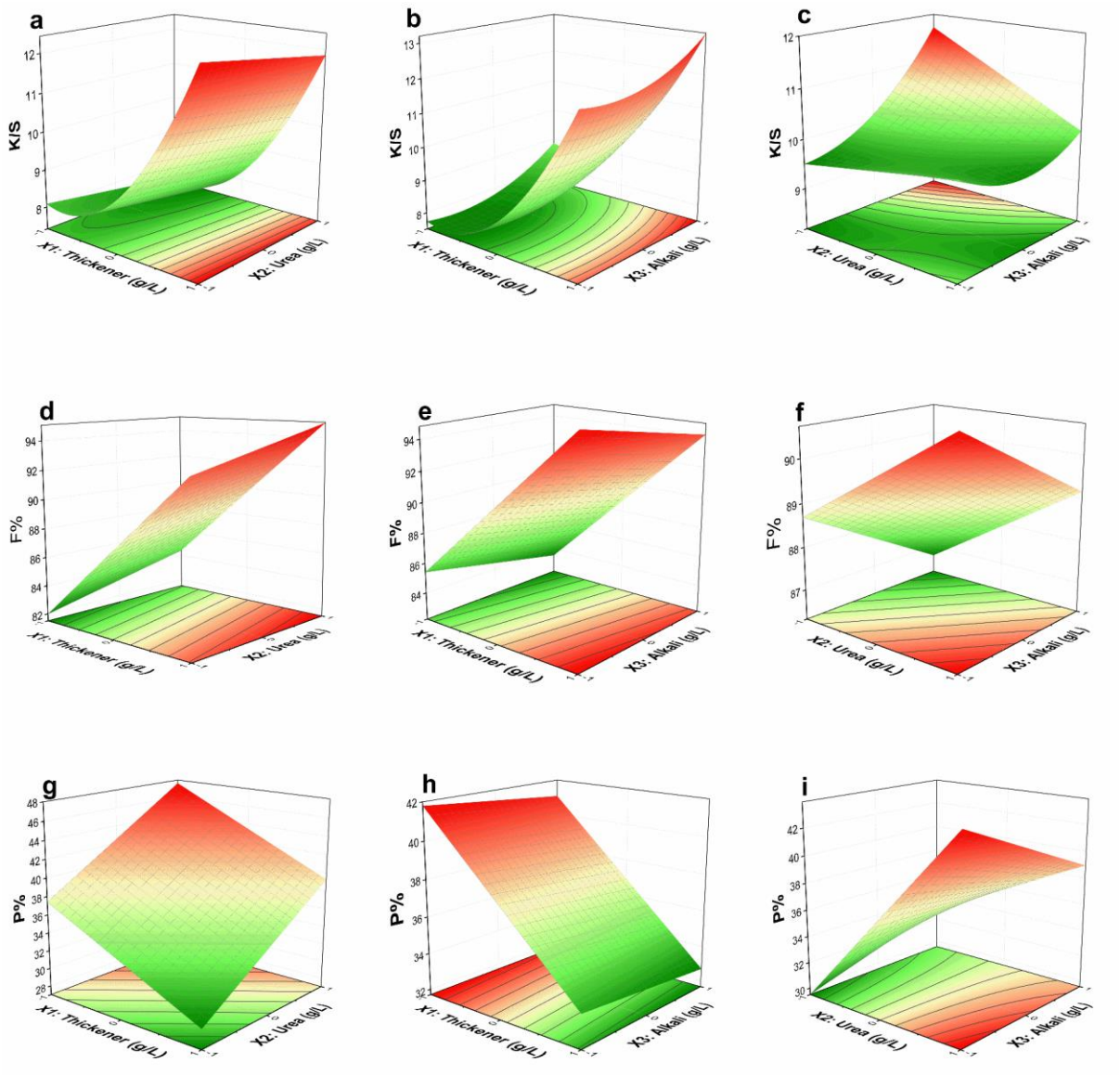

Figure 1: 3D response surface showing interactive effects of statistically significant ($p<0.05$) factors on K/S (a, b and c); F% (d, e, and f) and P% (g, h and i)

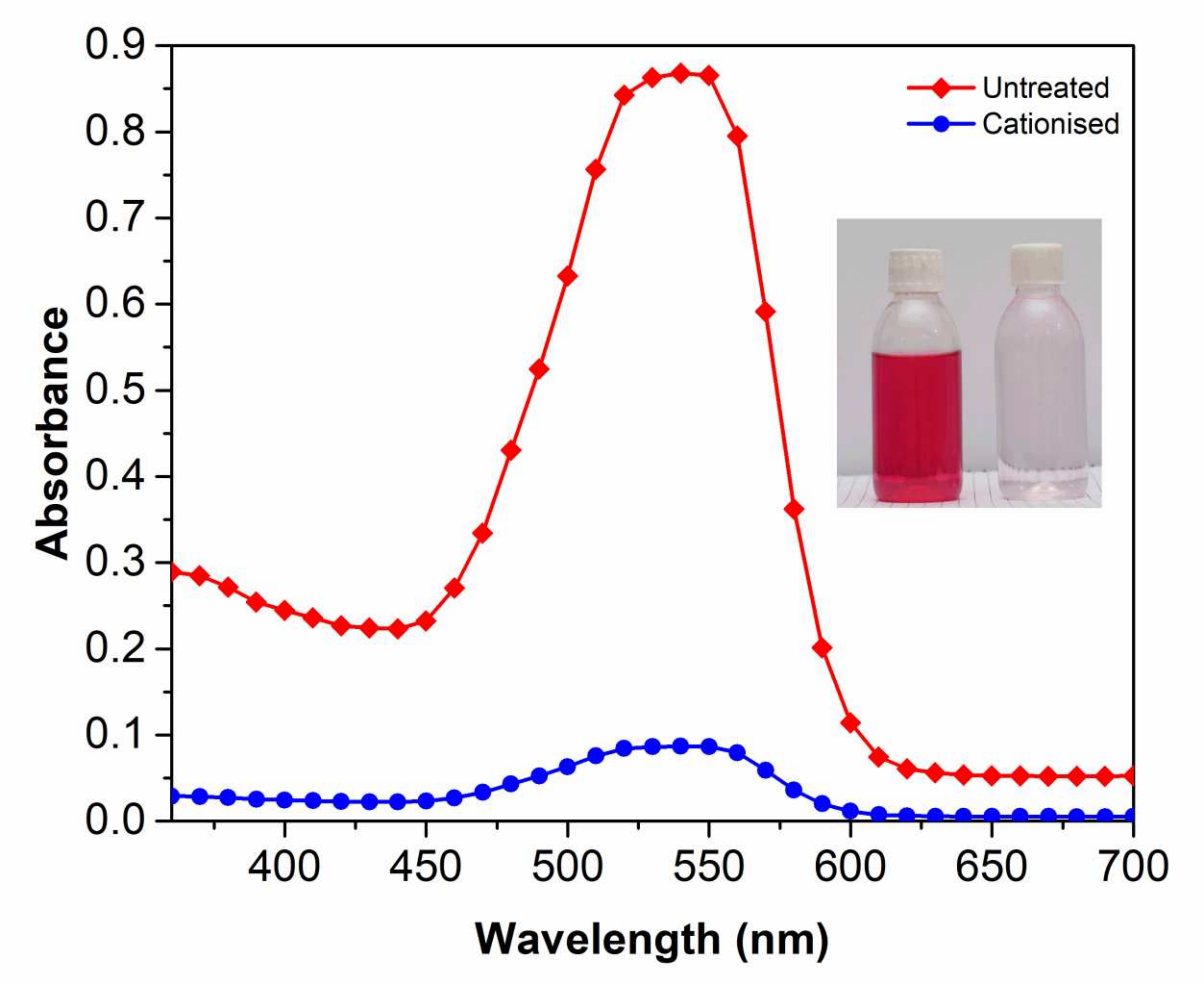

Figure 2: UV–Vis spectroscopy analysis of textile effluent generated from untreated and cationized digital-printed cotton

Table 1: Coded and uncoded values of independent variables

Symbol	Factors	Level		
		Low (-1)	**Center (0)**	**High (1)**
X1	Thickener (g/L)	150	175	200
X2	Urea (g/L)	75	100	125
X3	Alkali (g/L)	10	15	20

Table 2: Printing properties (K/S, F% and P%), digital images fastness properties and tear strength of untreated and cationized and digital-printed Cotton

Inkjet Printed Fabric	Color Strength (K/S)	Dye Fixation (F%)	Ink Penetration (P%)	Digital Images of Inkjet Printed Fabrics	Wash Fastness		Crock Fastness		Tear Strength (N)	
					Change in shade	Staining on cotton	Dry	Wet	Warp	Weft
Untreated	5.02	45.95	47.55		4	4-5	5	4.5	5.92	5.65
Cationized	12.55	95.24	39.13		4	4-5	5	4	5.85	5.58

Supplemental Material

https://doi.org/10.6084/m9.figshare.14300498

Statistical optimization and bulk scale validation of the effects of cationic pre-treatment of cotton fabric for digital printing with reactive dyes

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Screening Results

Amount of CHPTAC

To evaluate the printing properties of the digital-printed cotton fabrics, the samples were cationized with various amounts of CHPTAC (0, 25, 50, 75, 100 and 125 g/L) and then pretreated using 20 g/L of alkali, 200 g/L of urea, 180 g/L of thickener and 15 g/L Revatol S and subsequently steamed for 10 minutes. After digital printing, K/S, F% and P% values of all samples were calculated. The results are illustrated in Figures S1(a–c). The results of K/S and F% values [Figures S1 (a–b)] show that applying cationization drastically increased the K/S and F% of printed samples relative to the untreated and digital-printed cotton. This can be explained by the strong electrostatic attraction between the cationized cotton and the anionic reactive ink (Kanik and Hauser 2002). Also, the K/S and F% increased while increasing the amount of CHPTAC for cationization from 25 g/L to 75 g/L. This was because cationization

with higher amount of CHPTAC under alkaline conditions would enhance the substantivity and reactivity of the CHPTAC for cotton and lead to more cationic groups on the cotton fiber, thus enhancing ionic attraction between cationized fiber and anionic reactive ink (Wu and Chen 1992, Kanik and Hauser 2002). On the other hand, the results of P% values [Figure S1(c)] show that applying cationization decreased the P% of printed samples relative to the untreated and digital-printed cotton. This could be due to the decreased fabric porosity (due to the use of sodium hydroxide along with CHPTAC) and the strongly ionic attraction between anionic reactive ink and cationic charges on fibers. Similar results have been reported previously (Kanik and Hauser 2002, Kanik and Hauser 2004). In consideration of K/S and F%, 75 g/L of CHPTAC was chosen as the optimum amount for cationization since the K/S and F% leveled out with further increases in amount of CHPTAC.

Amount of Alkali

To evaluate the printing properties of the cationized and digital-printed cotton fabrics, the samples were cationized with 75 g/L of CHPTAC and then pretreated using various amounts of alkali (0, 5, 10, 15, and 20 g/L) along with 200 g/L of urea, 180 g/L of thickener and 15 g/L Revatol S and subsequently steamed for 10 minutes. After digital printing, printing properties were calculated for each sample and the results are illustrated in Figures S1(d–f). It can be seen from Figures S1(d and e), that the K/S and F% of cationized and digital-printed cotton samples significantly increased while increasing the amount of alkali from 0 g/L to 15 g/L. Further increase in amount of alkali decreased the K/S of cationized cotton and subsequently the F% also decreases. It is well known that alkali promote covalent bond formation between hydroxyl groups of cotton and reactive dye (Wu and Chen 1993, Faisal and Tronci 2018). However, for cationized cotton, higher amount of alkali can deprotonate the cationic amino groups which would decrease the cationized fiber's substantivity for the reactive dyes (Wu and Chen 1993). Thus, K/S and F% values of cationized and digital-printed cotton samples slightly affected

under highly alkaline conditions. On the other hand, the results of P% values [Figure S1(f)] show the decreasing trend with increasing amount of alkali. Thus, in consideration of printing properties, the optimum amount of alkali was chosen as 15 g/L for further studies.

Amount of Urea

To evaluate the printing properties of the cationized and digital-printed cotton fabrics, the samples were cationized with 75 g/L of CHPTAC and then pretreated using various amounts of urea (75, 100, 125, 150, 175 and 200 g/L) along with 15 g/L of alkali, 180 g/L of thickener and 15 g/L Revatol S and subsequently steamed for 10 minutes. Afterwards, printing properties were calculated for each sample and the results obtained are shown in Figures S1(g–i). It can be seen from Figures S1(g and h) that increasing amount of urea from 75 g/L to 100 g/L is accompanied by increase in K/S and fixation values. Further increase in amount of urea up to 200 g/L resulted in significant decrease in both K/S and F% values. One the other hand, P% increases with increasing amount of urea [Figure S1(i)]. This could be the reason which leads to lower K/S. Thus, 100 g/L of urea was chosen for further studies.

Amount of Thickener

To evaluate the printing properties of the cationized and digital-printed cotton fabrics, the samples were cationized with 75 g/L of CHPTAC and then pretreated using various amounts of thickener (100, 125, 150, 175 and 200 g/L) along with 100 g/L of urea and 15 g/L of alkali and 15 g/L Revatol S and subsequently steamed for 10 minutes. Afterwards, printing properties were calculated for each sample and the results obtained are shown in Figure S1(j–l). The K/S and F% increased with the increase in amount of thickener and maximum values were achieved at 175 g/L of thickener. The further increase in the amount of thickener resulted in a significant decrease in both K/S and F%. Moreover, the P% values are consistent with the previous results. Thus, 175 g/L of thickener was selected for further investigations.

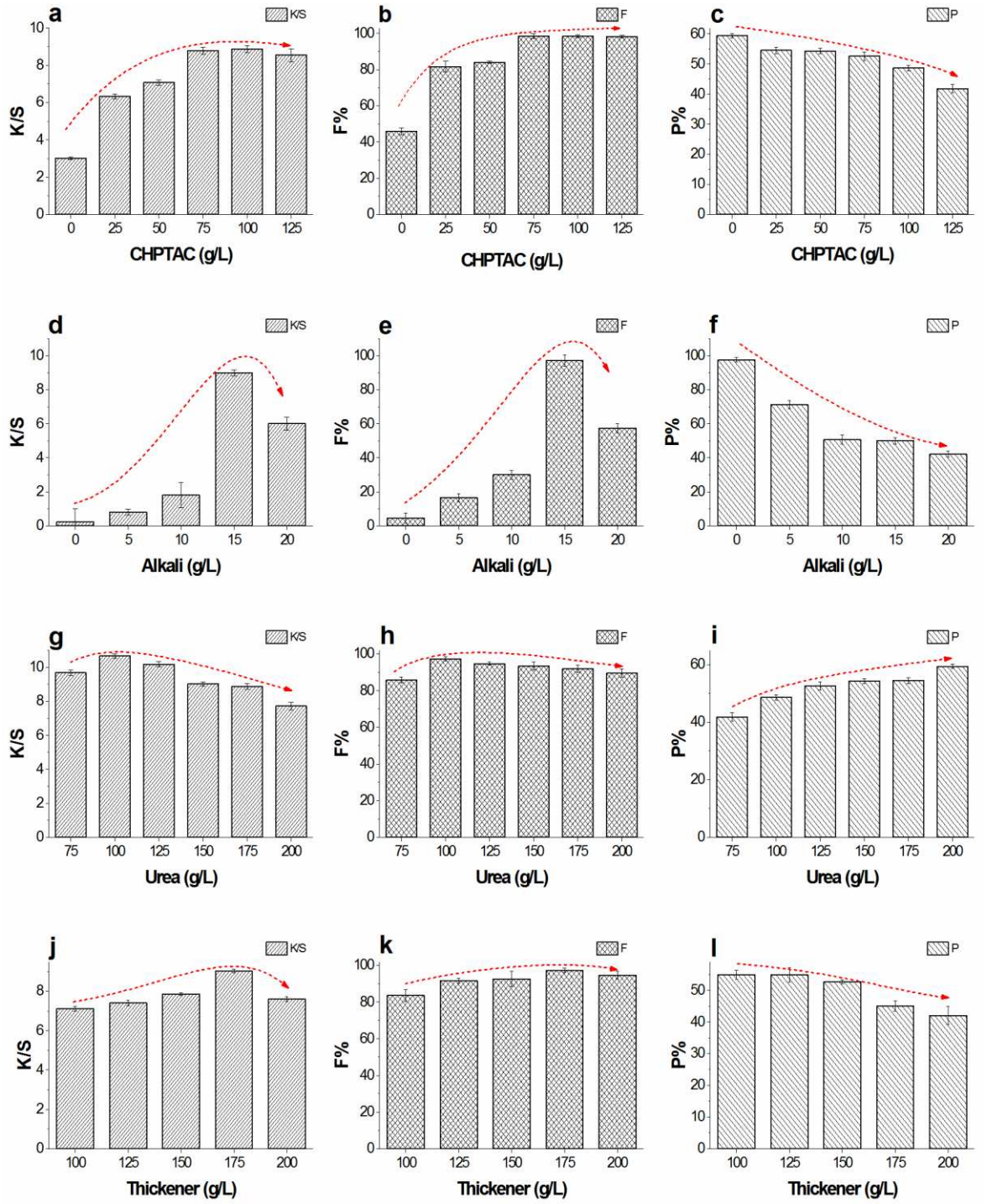

Figure S1: Effect of amount of CHPTAC (a, b, and c), amount of alkali (d, e and f), amount of urea (g, h and i) and amount of thickener (j, k and l) on printing properties of cationized and inkjet-printed cotton

Table S1: Design matrix and experimental results

Run Order	Factors			K/S	F%	P%
	X_1	X_2	X_3			
1	1	1	0	11.98	93.83	35.03
2	-1	-1	0	8.10	82.01	35.00
3	1	0	1	13.40	92.24	31.18
4	0	-1	1	10.24	86.01	31.77
5	0	1	-1	8.91	91.82	45.50
6	1	-1	0	12.44	92.85	28.33
7	1	0	-1	11.72	95.75	32.51
8	0	0	0	8.38	88.32	36.73
9	0	1	1	8.53	90.10	39.53
10	0	-1	-1	8.43	88.33	29.49
11	-1	0	1	8.96	83.40	41.04
12	-1	1	0	7.53	83.12	45.31
13	-1	0	-1	7.61	83.65	39.00
14	0	0	0	8.66	87.82	35.70
15	0	0	0	8.32	88.31	38.20

Table S2: ANOVA for reduced models for the printing properties (K/S, F% and P%) of cationized and digital-printed cotton

Source	SS	df	MS	F-value	*p*-value	Remarks
K/S						

Model	50.53	6	8.42	147.95	< 0.0001	significant
X1-Thickener	37.61	1	37.61	660.65	< 0.0001	
X2-Urea	0.6362	1	0.6362	11.18	0.0102	
X3-Alkali	2.49	1	2.49	43.82	0.0002	
X2X3	1.20	1	1.20	21.10	0.0018	
$X1^2$	8.04	1	8.04	141.31	< 0.0001	
$X3^2$	0.8849	1	0.8849	15.55	0.0043	
Residual	0.4554	8	0.0569			
Lack of Fit	0.3880	6	0.0647	1.92	0.3815	not significant
Pure Error	0.0674	2	0.0337			
Cor Total	50.98	14				
$R^2 = 0.9911$, $R^2_{(adj)} = 0.9844$ and $R^2_{(pre)} = 0.9492$						
F%						
Model	245.068	3	81.689	91.17	<0.0001	significant
X1-Thickener	225.771	1	225.771	251.96	<0.0001	
X2-Urea	11.698	1	11.698	13.06	0.004	
X3-Alkali	7.599	1	7.599	8.48	0.014	
Residual	9.857	11	0.896			
Lack of Fit	9.690	9	1.077	12.97	0.074	not significant
Pure Error	0.166	2	0.083			
Cor Total	254.925	14				
$R^2 = 0.9613$, $R^2_{(adj)} = 0.9508$ and $R^2_{(pre)} = 0.9193$						
P%						
Model	364.64	4	91.16	46.04	< 0.0001	significant

X1-Thickener	138.84	1	138.84	70.12	< 0.0001	
X2-Urea	207.68	1	207.68	104.89	< 0.0001	
X3-Alkali	1.12	1	1.12	0.5644	0.4698	
X2X3	17.01	1	17.01	8.59	0.0150	
Residual	19.80	10	1.98			
Lack of Fit	16.64	8	2.08	1.32	0.5007	not significant
Pure Error	3.16	2	1.58			
Cor Total	384.44	14				
$R^2 = 0.9484$, $R^2_{(adj)} = 0.9277$ and $R^2_{(pre)} = 0.8640$						

* SS – Sum of squares; ** MS – Mean square

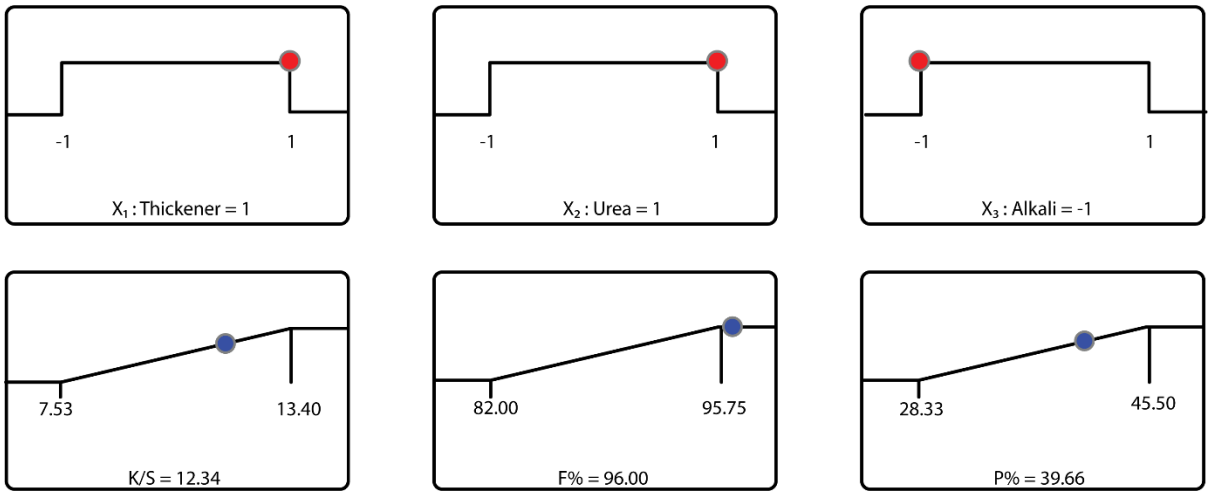

Figure S2: Desirability ramp for optimization of printing properties of cationized and digital-printed cotton fabric

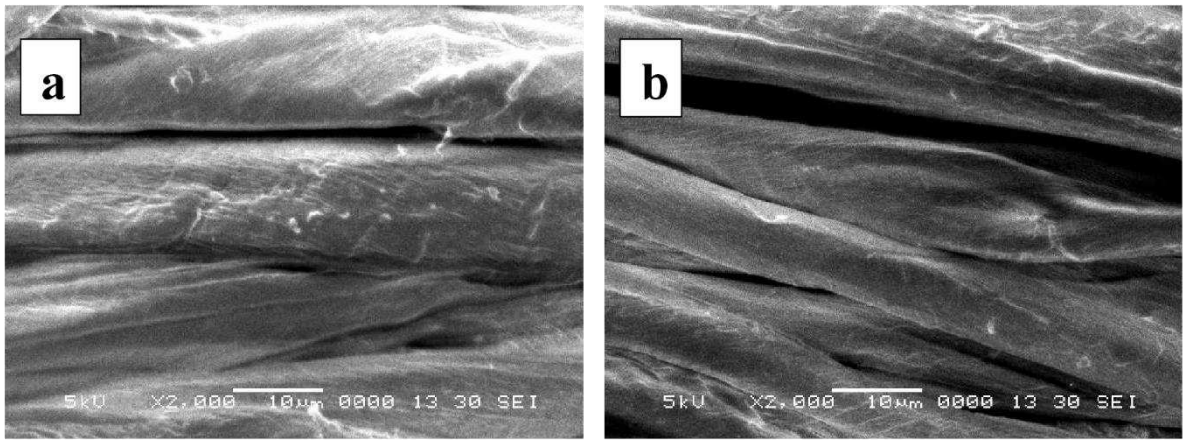

Figure S3: SEM images of untreated (a) and cationized cotton (b)

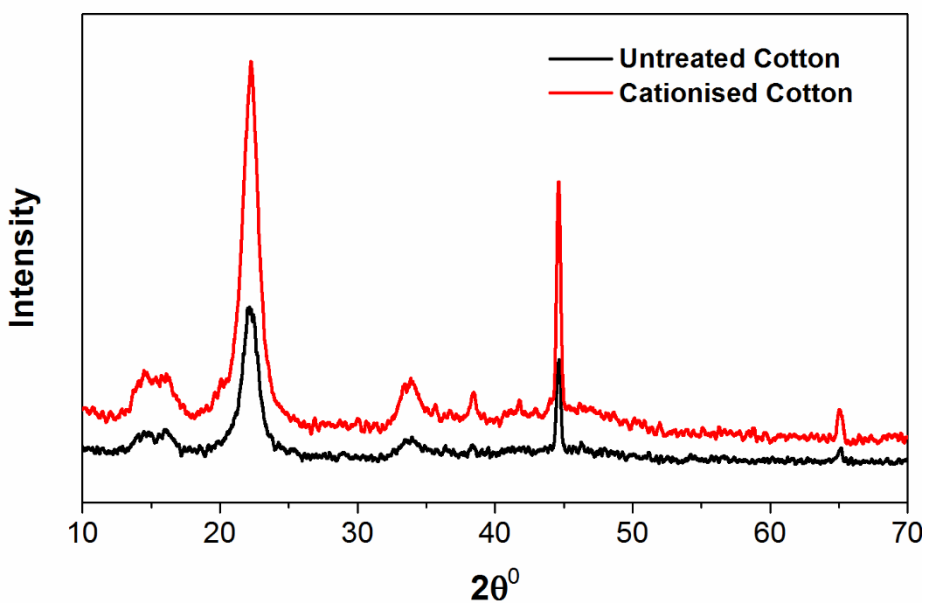

Figure S4: XRD spectra of untreated and cationized cotton

Table S3: Economic analysis of the proposed optimised cationization of cotton fabric

Cost of Cationization	
GSM of selected substrate	130
GLM (for 60-inch fabric width)	198.12
Fabric Weight (per meter)	0.198 kg/m
Length of fabric in 100 kg	505 m
Cationic pre-treatment cost	Rs 15/m
Cationic pre-treatment cost for 100 kg (or 505 m) of fabric	A = Rs 7575

Liquor volume consumed for 100 kg (or 505 m fabric) @ 75% pickup	75 L
Amount of CHPTAC in 75 L liquor (Recipe; 75 g/L)	5.625 kg
CHPTAC Unit price	Rs 400 /kg
Amount of NaOH in 75 L liquor (Recipe; 47 g/L)	3.525 kg
NaOH Unit price	Rs 200 /kg
Cost of chemicals used for Cationization	B = (5.625x400) + (3.525x200) B = Rs 2966
Total cost of cationic pre-treatment for 100 kg (505 m) fabric	C = A + B C = Rs 10541
Savings in terms of reduction in the amount of hydrolysed dye	
Cost of dye	Rs 2185/L
Dye consumption	50 mL/m of fabric
Cost of dye per meter of fabric	Rs 109.25
Cost of Dye for 100 Kg (or 505 m) of fabric	Rs 55171
At 46% fixation, cost of hydrolysed dye	D = 0.54 x 55171 = Rs 29792
At 95% fixation, cost of hydrolysed dye	E = 0.05 x 55171 = Rs 2758
Overall economic benefit	
Dye saving in terms of hydrolysed dye (per 100 kg fabric)	F = D – E = Rs 27034
Net savings per 100 kg (or 505 m) of fabric	G = F – C G = Rs 16493
Average production per day	H = 7200 m
Savings per day for the substrate considered	I = Rs 235148 (USD 1495)

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