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KATYONİKLEŞTİRME İŞLEMİNİN ATIK SU KARAKTERİZASYONU, PAMUKLU KUMAŞIN FİZİKSEL VE HASLIK DEĞERLERİ ÜZERİNE ETKİSİNİN İNCELENMESİ

INVESTIGATION OF THE EFFECT OF CATIONIZATION PROCESS ON WASTEWATER CHARACTERIZATION, PHYSICAL AND FASTNESS VALUES OF COTTON FABRIC

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INVESTIGATION OF THE EFFECT OF CATIONIZATION PROCESS ON WASTEWATER CHARACTERIZATION, PHYSICAL AND FASTNESS VALUES OF COTTON FABRIC

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ABSTRACT: Reactive dyeing is the most widely used dyeing method for dyeing cellulosic fabrics in the textile industry. In this study, it was aimed to reduce the environmental impact caused by the use of high salt during the dyeing of cellulosic fabrics with reactive dyestuffs. In this context, a quaternary ammonium based chemical was used for the cationization of cotton fabrics. The usage amount of cationizing agent and flake caustic was determined with the experiments as 50 g/L and 17 g/L, respectively. Conventional and salt-free dyeing of standard fabric and salt-free dyeing of cationic fabric were carried out with 8 different 1% reactive dyestuffs in the laboratory. As a result of dyeing, it was observed that the color strength of cationic fabrics was at least as high as conventional dyeing. Pilot-scale trials were conducted with black color, the most commonly used dye in production. Two different dyeing processes, conventional dyeing of standard fabric and salt-free dyeing of cationic fabric, were carried out using 7% black reactive dyestuff. The findings revealed that cationic fabric has 8.6% darker color than standard fabric. Fastness and strength values were similar for both fabrics. the Total Dissolved Solids (TDS) value of the salt-free dyeing bath was 74.4 % lower than conventional dyeing. Similarly, the conductivity value of salt-free dyeing was 73% and the Chemical Oxygen Demand (COD) value was 27.8% lower when compared with conventional dyeing bath results. At the end of these studies, it has been seen that the same color strength can be obtained with less dyestuff by using the cationization process and the waste water load can be reduced.

Keywords: Salt-Free dyeing, amino compounds, eco-friendly dyeing, fabric cationazition

KATYONİKLEŞTİRME İŞLEMİNİN ATIK SU KARAKTERİZASYONU, PAMUKLU KUMAŞIN FİZİKSEL VE HASLIK DEĞERLERİ ÜZERİNE ETKİSİNİN İNCELENMESİ

ÖZET: Reaktif boyama**,** tekstil endüstrisinde selülozik kumaşların boyanmasında en yaygın kullanılan boyama yöntemidir. Çalışma ile selülozik kumaşların reaktif boyarmaddelerle boyanması sırasında yüksek miktarda tuz kullanımının yol açtığı çevresel etkinin azaltılması amaçlanmıştır. Bu kapsamda, pamuklu kumaşların katyonikleştirilmesi için kuaterner amonyum türevi bir kimyasal kullanılmıştır. Çalışmada kullanılacak katyonikleştirme ajanı ve pul kostik miktarı yapılan denemelerle sırasıyla 50 g/L ve 17 g/L olarak belirlenmiştir. Laboratuvarda 8 farklı %1 oranında reaktif boyarmadde ile standart kumaşın konvansiyonel ve tuzsuz boyanması, katyonik kumaşın tuzsuz boyanması gerçekleştirilmiştir. Boyamalar sonucunda katyonik kumaşların renk kuvvetinin en az konvansiyonel boyama kadar yüksek olduğu görülmüştür. Pilot ölçekli denemeler, işletmede en çok kullanılan boya olan siyah ile yapılmıştır. %7 siyah reaktif boyarmadde kullanılarak standart kumaşa konvansiyonel boyama ve katyonik kumaşa tuzsuz boyama olmak üzere iki farklı boyama işlemi gerçekleştirilmiştir. Sonuç olarak, katyonik kumaşların, standart kumaşlara göre %8.6 daha koyu renge sahip olduğu görülmüştür. Haslık ve mukavemet değerleri her iki kumaş için de benzerdir. Boyama banyolarının atık su analizleri sonucunda tuzsuz boyama banyosunun konvansiyonel boyamaya göre toplam çözünmüş katı madde değeri %74.4, iletkenlik değerleri %73 ve kimyasal oksijen ihtiyacı (KOİ) değeri %27.8 daha düşüktür. Yapılan çalışmalar neticesinde katyonikleştirme işlemi ile daha az boyarmadde ile aynı rengin elde edilebildiği ve atık sudaki yükün düşürülebildiği görülmüştür.

Anahtar Kelimeler: Tuzsuz boyama, amino bileşikler, çevre-dostu boyama, kumaş katyonizasyonu

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1. INTRODUCTION

There is a potential for high water consumption and wastewater in wet processes in the textile industry [1]. Reactive dyestuffs are frequently used in dyeing cellulosic fabrics for good washing fastness and wide bright color pallete [2, 3]. Due to the moderate affinity of reactive dyestuffs to cotton, water usage and environmental pollution are high. High concentrations of electrolytes (sodium sulfate and sodium chloride) are used in the dyebath to increase the affinity of the dyestuff to the fabric [4, 5]. Electrolyte usage rate varies between 10-100 g/L depending on the percentage of dyestuff [6].

High-cost treatment processes are required for the treatment of salty and colored wastewater [2]. Also, treatment and reuse of wastewater cause difficulties due to the high total dissolved solids (TDS), color and chemical oxygen demand (COD) values and different pH values [7, 8]. Reducing the amount of water used in the textile industry can be provided by innovations in different areas such as textile machinery, textile processes, chemicals and auxiliaries except treating and reusing of textile waste water [9].

There are different developments for reactive dyeing systems to improve wastewater quality, reduce or eliminate salt. These developments are as follows:

• Development of reactive dyes
• Development of dyeing machines and processes
• Cationization of cotton
• Use of biodegradable organic ingredients in the dyeing bath
• Development of wastewater treatment processes [5]

Among these studies the cationization of cotton is the practical way that can be adapted to industrial scale production [10, 11]. Cationization of cellulose is a chemical treatment that modifies the cellulose molecule, making it strongly cationic. This pretreatment increases the affinity between cotton and anionic dyes [12]. To incorporate cationic sites by reaction with hydroxyl groups of cellulose through esterification, etherification, grafting or crosslinking reaction is termed as cationization of cotton [13]. Basically quaternary or tertiary amino groups are embodied with cellulose to provide nucleophilic group to cellulose which show greater attraction for anionic dye resulting in formation of ionic bond without salt even alkali [14]. The chemicals used in cotton cationization are separated into two groups: Low molecular weight cationic agents [10, 11] and polymeric cationic agents [11, 15]. The most common approach for cationization is to treat cotton using various amino compounds. An attraction occurs between amino groups and anionic dyes with a positive charge on cellulosic fibers, resulting in high durability for dyes [16, 17].

Cellulosic fibers have a negative change when they come into contact with water. Reactive dyes are anionic. So low exhaustion rate between cotton and reactive dyes is increased by using salt. Thanks to the cationization process, a strong attraction occurs between the treated cotton fabric and reactive dye which led to obtaining very high exhaustion rates without the addition of electrolytes to the dye bath.

When the cationizing agent was treated to cotton fabric, it reacts with cotton fibre to make quaternary ammonium salt on the surface of fibre and enables union of cationized cotton fibre with anionic dye by ionic bondage [18]. The quaternary ammonium group has a persistent positive charge and can thereby lead to the formation of ionic bonds with negatively charged anionic groups, such as those found in a wide array of anionic dye classes or carboxy-containing compounds [13]. Probable reaction of cationizing agent was shown in Figure 1.

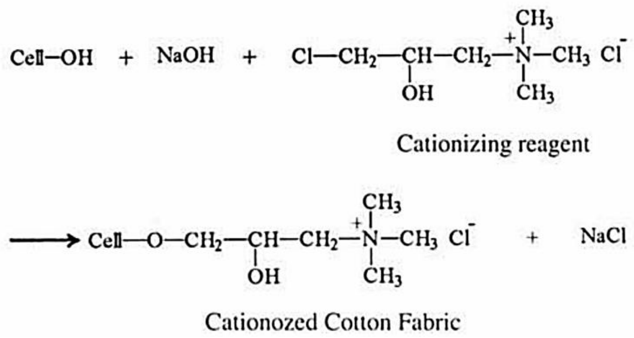

Figure 1. Probable reaction of cationizing agent with cotton fabric [18]

In the research conducted, it is seen that compounds containing trimethyl ammonium chloride in its structure such as various amino compounds, epichlorohydrin compounds and derivatives, 3-chloro-2-hydroxy-propyl trimethyl ammonium chloride are used [19, 20]. There are also studies with chitosan and dendrimer compounds.

With the cationization process of cotton, higher color yield is obtained at the same dye rates and less rinsing is required after dyeing. It is a more environmentally friendly process since the use of salt in dyeing baths can be avoided [19, 20].

In the studies carried out on the subject, the padding method was mostly used. Cationization processes were carried out at room temperature in 24 hours, and the cationic agent was used between 35-50 g/l. Caustic was used in the range of 15-20 g/l. In all studies, it was observed that cationic fabrics were dyed darker and there was no problem in fastness. In these studies, reactive, direct and acid dyes were used [16-21]. There are also successful studies in which cationic fabric was dyed in reactive and direct dyestuffs in an acidic environment without salt and soda [4].

Although the fabric cationization process looks promising, most of the studies have been carried out with the cold pad batch process. However, the exhaustion method is used more frequently in the sector [22-25]. In another study conducted by Arivithamani and Giri Dev (2017a), cotton knitted fabric was cationized according to the exhaustion method. As a result of the trials, it was obtained desired fastness values and even dyed fabrics. It has been observed that when a color was stripped from fabric and fabric was redyed with the same recipe without using salt, it was seen that no significant color difference occurred in the redyed fabric [2].

There were also studies conducted with cationic starch, chitosan and dendrimer apart from CHPTAC to cationize the fabric. Fabrics treated with chitosan and cationic starch were dyed without salt. Results showed that higher K/S values were obtained when compared with dyeing using salt [26, 27]. In a study using dendrimer, it was seen that there were trials where darker colors were obtained than conventional dyeing in dyeing at different pH values without using salt and soda [28].

The aim of this study is to reduce the total dissolved solids content, conductivity and color in wastewater by providing high fixation thanks to the new salt-free process developed, and to develop a more environmentally friendly reactive dyeing process without compromising the fastness values of the fabric. For this purpose, fabric cationization was carried out using quaternary ammonium-based chemicals.

In order to evaluate the environmental effects of the application, unlike the studies conducted in the literature, some parameters of wastewater characterization such as the total dissolved solids (TDS), chemical oxygen demand (COD), color and conductivity values of the wastewater samples taken from of each bath were compared with conventional dyeing in this study. Color strength and fastness values were compared with conventionally dyed fabrics. In this study, pilot-scale trial results that run in the production site were also shared. In addition, the use of dyestuffs with different color indexes, which has not been studied in the literature before, is another innovative aspect of the study.

2. MATERIAL AND METHOD

2.1. Material

A ready for dyeing woven fabrics of 108 g/m^2 100% cotton was chosen to be used in the study. A quaternary ammonium-based chemical was chosen for the cationization process and obtained from a Taiwan-origin chemical company called JINTEX Corporation Ltd.. Flake caustic was also used in the cationization bath and supplied by Koruma Klor Alkali San. ve Tic. A.Ş.. Ion immobilizer, levelling agent, anti-creasing agent, soap and acetic acid as neutralization acid were used as auxiliaries and can be supplied by any company that sells textile auxiliaries. Reactive dyestuffs used in the study and their properties have given in Table 1.

THERMAL branded water bath was used in studies carried out at laboratory-scale. For pilot-scale production, a 20 kg capacity “Fongs” branded jet dyeing machine was used.

2.2. Metod

2.2.1. Cationization processes

Laboratory-scale optimisation studies were carried out in 1:10 liquor in the water bath with 7% black dyestuff. In the trials, the usage amount of the cationization agent was determined first. 10 g/L, 30 g/L, 50 g/L and 70 g/L cationization agents were tried in the trials, respectively. In these pre-treatment baths, the amount of caustic was used as 3 g/L, 10 g/L, 17 g/L and 23 g/L, respectively, at a ratio of 1/3 of the cationization agent. Then, in order to determine the amount of caustic, experiments were carried out using 50 g/L cationization agent with no caustic, 8 g/L and 17 g/L caustic. The cationization process was carried out to fabrics 60ºC for 50 minutes. Then the fabric was rinsed at 30ºC for 10 minutes and neutralized at 30ºC by using 1 g/L acetic acid for 15 minutes.

The cationization process in pilot-scale trials was carried out in a jet dyeing machine in 1:10 liquor. In the cationization process, 50 g/L catonization agent and 17 g/L caustic were used. Cationization process diagram was shown in Figure 2.

2.2.2. Dyeing processes

In laboratory-scale dyeing trials, dyeing was carried out with 1% dyestuffs in 1:20 bath ratio. In the conventional dyeing process, 0.8 g/L ion immobilizer, 0.5 g/L anti crease agent, 0.5 g/L leveling, 65 g/L salt and 12 g/L soda ash were used. In the salt-free dyeing process, the same chemical amounts were used except salt. Dyeings was carried out at 60ºC for 60 minutes. After the dyeing step, washings were carried out as following steps: rinsing at 60ºC for 10 minutes two times, neutralization at 50ºC for 10 minutes with 1 g/L acetic acid, soap washing at 95ºC for 15 minutes with 0.5 g/L soap, neutralization at 40ºC for 10 minutes with 1 g/L acetic acid.

In pilot scale trials, cationized and salt-free dyed fabric was compared with standard and conventionally dyed fabric. 7% black color dyeing was performed in the jet machine. The conventional dyeing process in the jet machine was given in Figure 3.

Table 1. Reactive dyestuffs used in the trials and their properties

COLOR INDEX	REACTIVE GROUP	CHROMOPHORE GROUP
BLACK MIX	Monochlorotriazine	AZO
RED 195	Monochlorotriazine & Vinyl sulfone	AZO
YELL 145	Monochlorotriazine & Vinyl sulfone	AZO
BLUE 221	Monochlorotriazine & Vinyl sulfone	AZO
UNKNOWN (ORANGE)	Monochlorotriazine & Vinyl sulfone	AZO
RED 278	Monochlorotriazine & Vinyl sulfone	AZO
UNKNOWN (NAVY)	Monochlorotriazine & Vinyl sulfone	AZO
BLUE 21	Vinyl sulfone	AZO

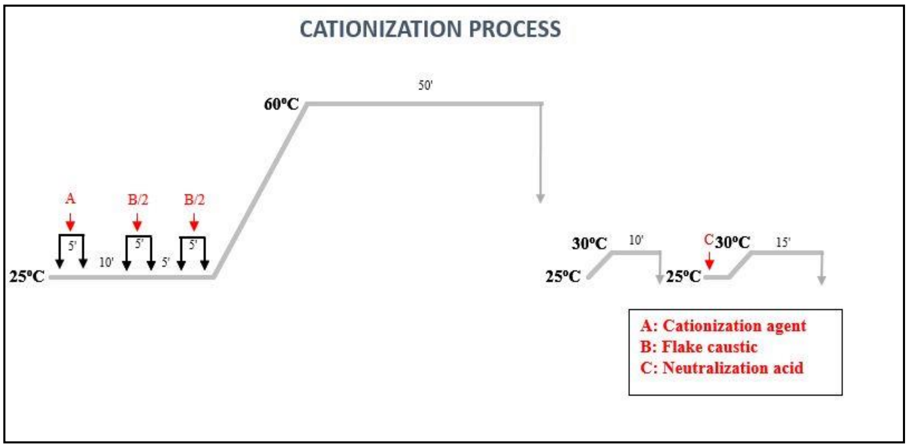

Figure 2. Cationization process diagram

The dyeing of the cationized fabric with 50 g/L cationization agent and 17 g/L flake caustic was carried out according to salt-free dyeing process given in Figure 4. The only difference between the salt-free dyeing process and the conventional reactive dyeing process is that no salt is used in the dyeing process.

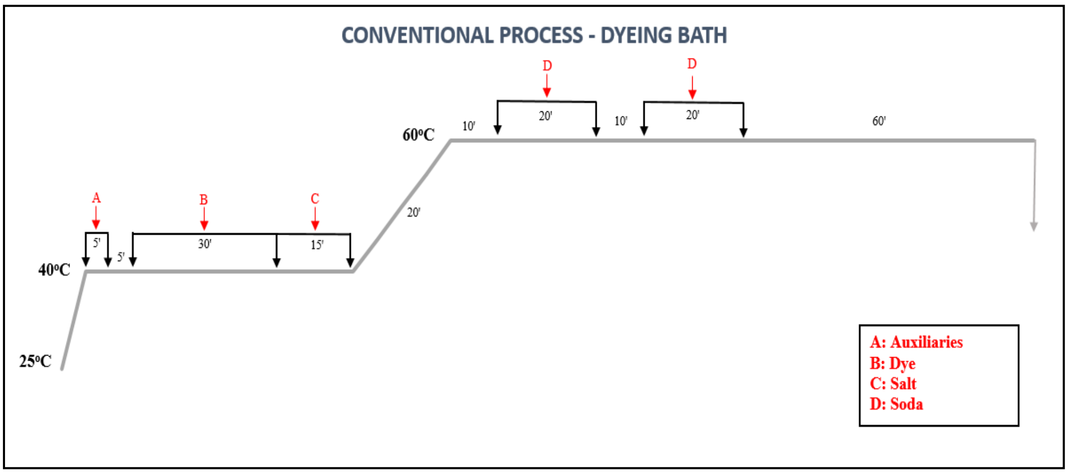

Figure 3. Conventional dyeing process diagram

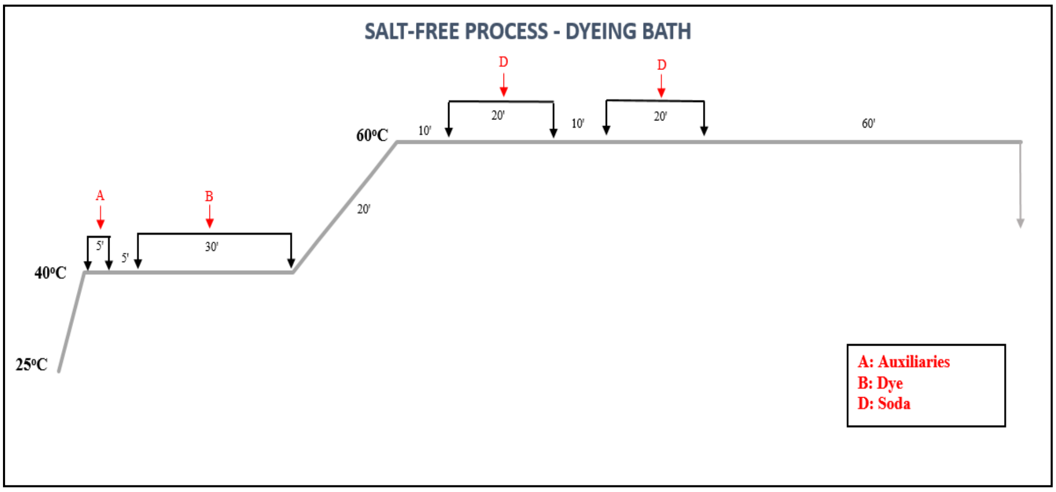

Figure 4. Salt-free dyeing process diagram

Washing baths after dyeing were the exactly the same for both dyeing processes (see Figure 5). There was two rinsing bath at 60°C for 10 minutes. After that, fabrics were neutralized by using 1 g/l acetic acid at 50°C for 10 minutes. Then two washing baths were achieved at 95°C for 15 minutes by using 0.5 g/l soap. Finally, the fabrics were neutralized by using 1 g/l acetic acid at 40°C for 10 minutes.

2.2.3. Color measurements

Color strength analysis measurements for dyed fabrics were carried out with a Datacolor 1050 model spectrophotometer. Measurements were made according to the CIELab color space under D_{65} illuminant, using a 10° standard observer at 6.6 mm aperture. From the reflectance values (R) in the visible spectrum (400–700 nm) at the maximum absorption wavelength (λmax) for each dye, the corresponding color strength (K/S) values of the samples were examined [29].

The CIE in CIELAB is the abbreviation for the International Commission on Illumination's French name, Commission Internationale de l´Eclairage. The letters L*, a* and b* represent each of the three values the CIELAB color space uses to measure objective color and calculate color differences. L* represents lightness from black to white on a scale of zero to 100, while a* and b* represent chromaticity with no specific numeric limits. Negative a* corresponds with green, positive a* corresponds with red, negative b* corresponds with blue and positive b* corresponds with yellow [30].

2.2.4. Fastness tests

Washing fastness tests were carried out in James Heal branded gyrowash machine according to ISO 105-C06:2010 A2@40°C standard [31]. The results were evaluated according to the gray scale. Perspiration fastness and water fastness tests were carried out in Nuve branded oven according to ISO 105-E04:2013 standard and ISO 105-E01:2013 standard, respectively [32, 33]. The results were evaluated according to the gray scale. Light Fastness test was carried out according to ISO 105-B02:2014 Metot 2 Blue Wool Grade 4 [34]. Rubbing Fastness was made in James Heal branded friction fastness tester according to ISO 105X12:2006 standard [35]. The results were evaluated according to the gray scale.

2.2.5. Waste water analysis

COD values of cationization and dyeing process wastewaters were measured according to Closed Reflux, Colorimetric Methods (5220D) by using Hach branded UV/VIS spectrophotometer [36]. Conductivity values are measured by using Hach branded conductivity meter. Total Dissolved Solids (TDS) values were calculated according to the correlation between conductivity and TDS [37]. Color measurement of wastewater were conducted by using Hach branded UV/VIS spectrophotometer according to ASTM D1209-05 [38].

3. RESULTS AND DISCUSSION

3.1. Color Measurements

Color measurements of cationization agent optimization studies performed in the laboratory were given in Table 2. When the L, a and b values are examined, it is seen that as the amount of cationization agent used increases, the darkness, redness and yellowness increase, respectively. The K/S values are 24.49 for 50 g/L of the cationizing agent, and the K/S value is 24.77 for 70 g/L. It was seen that there was no significant difference regarding K/S values between the use of 50 g/L and 70 g/L cationization agents. So the amount of cationization agent used was determined as 50 g/L.

Table 3 gives the CIELAB results obtained from the studies carried out to reduce the amount of flake caustic in the cationization process. When Table 3 was examined, it was seen that the L value decreases, and the a and b values increased with the increase in the amount of flake caustic. Similar to the cationization agent amount determination, in the experiments with flake caustic, it is seen that there is a direct proportionality between the amount of flake caustic and the darkness, redness and yellowness. The highest K/S value of 24.72 was obtained by using 17 g/L flake caustic. While the K/S value was 16.79 without flake caustic, it was 17.54 when flake caustic was used 8 g/L. Color strength decreased when the flake caustic ratio was decreased. Therefore, the cationization recipe was determined as 50 g/L cationization agent and 17 g/L flake caustic.

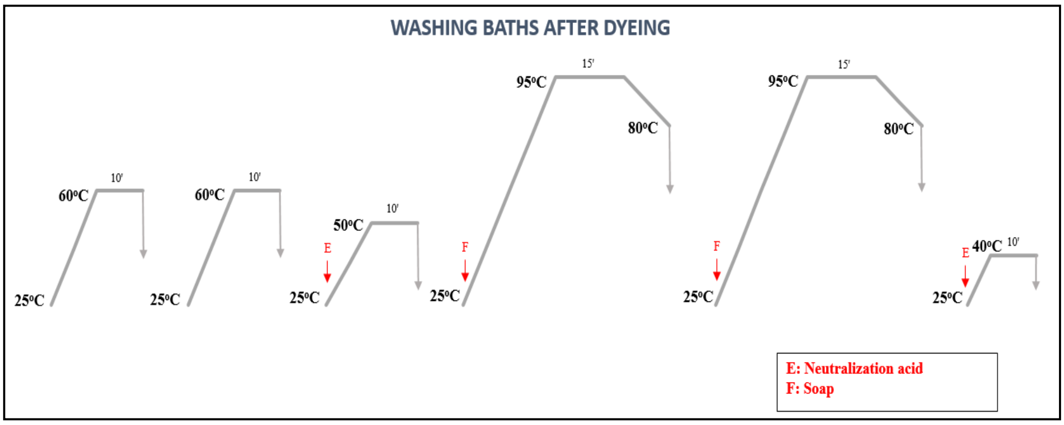

Figure 5. Washing baths after dyeing diagram

Table 2. Cationization agent optimization results

	L	a	b	C	h	ΔE	K/S
10 g/L Cationizing Agent	20.46	-0.08	-3.71	3.72	268.69	Referance	18.51
30 g/L Cationizing Agent	18.51	0.22	-2.43	2.44	275.28	2.21	21.01
50 g/L Cationizing Agent	16.46	0.32	-1.72	1.74	280.50	4.03	24.49
70 g/L Cationizing Agent	16.06	0.59	-1.11	1.25	297.97	4.86	24.77

Table 3. Flake caustic determination experiments result

	L	a	b	C	h	ΔE	K/S
Without Flake Caustic	21.83	-0.36	-4.36	4.37	265.23	Referance	16.79
8 g/L Flake Caustic	20.92	0.04	-3.55	3.55	270.60	3.44	17.54
17 g/L Flake Caustic	15.97	0.57	-0.95	1.11	300.93	5.07	24.72

After the cationization recipe was determined, dyeing trials were carried out for all colors. Laboratory dyeings were carried out as standard fabric - conventional dyeing (SF-CD), standard fabric - salt-free dyeing (SF-SFD) and cationic fabric - salt-free dyeing (CF-SFD). The spectrophotometer results of 3 different dyeing experiments for each color were given in Table 4. When the **ΔE** values examined, it can be seen that almost the same color is obtained with conventional dyeing in Black Mix, Red 278 and Navy colors. When the dyeings made with the SF-CD process type was compared to the CF-SFD process type for Black Mix, Red 278 and Navy colors, the **ΔE** values are 0.28, 0.78 and 0.35, respectively. Since the **ΔE** value is below 1 point, it can be said that there is no significant difference between the salt-free dyeing of the cationic fabric and the conventional dyeing in which the standard fabric is dyed with salt.

It was seen that higher K/S values were obtained in CF-SFD trials except Navy color. Especially in Blue 221, the K/S value of SF-CD was 3.95 and the K/S value of CF-SFD was 6.38. That means up to 60% darker colors can be obtained by using the cationization process in a jet dyeing machine.

All SF-SFD fabrics have higher L values than other process types. This indicates that SF-SFD fabrics have a lighter color. There is a difference from color to color between the dyeing process and the a and b values. For this reason, no correlation was observed between the cationization process and the chromaticity. Although the cationization process was applied to the fabrics by using the same method, it was seen that different dyestuffs were affected at different rates. This shows that the success of the process also depends on the dyestuff. In the studies carried out in the literature, it has been observed that cationic dyeing can obtain 1.5 to 3.5 times darker color than conventional dyeing in cationization studies performed with the padding method [16, 21].

Table 4. Colorimetric parameters for all dyeings in laboratory

COLOR INDEX	PROCESS TYPE	L	a	b	C	h	ΔE	K/S
BLACK MIX	SF-CD	31,32	-1.00	-5.95	6.03	260.48	Referance	8.35
	SF-SFD	40.40	-0.89	-5.27	5.34	260.44	5.53	4.35
	CF-SFD	30.49	0.41	-4.66	4.68	275.08	0.28	8.50
RED 195	SF-CD	56.65	48.98	-4.82	49.21	354.38	Referance	3.10
	SF-SFD	59.77	46.04	-5.36	46.35	353.36	1.81	2.32
	CF-SFD	53.68	50.98	-3.54	51.10	356.03	1.68	4.04
YELL 145	SF-CD	79.37	20.96	71.04	74.07	73.56	Referance	5.01
	SF-SFD	82.70	16.92	64.27	66.46	75.25	3.12	3.01
	CF-SFD	77.32	24.27	73.34	77.25	71.69	2.11	6.45
BLUE 221	SF-CD	49.94	-2.94	-29.40	29.54	264.29	Referance	3.95
	SF-SFD	54.77	-3.46	-27.00	27.22	262.70	2.58	2.69
	CF-SFD	43.56	-1.94	-30.46	30.52	266.36	3.10	6.38
UNKNOWN (ORANGE)	SF-CD	63.05	44.99	59.87	74.89	53.08	Referance	8.56
	SF-SFD	66.38	41.21	55.92	69.46	53.61	2.77	5.67
	CF-SFD	61.71	45.99	62.57	77.65	53.68	1.11	10.75
RED 278	SF-CD	40.38	49.43	9.92	50.42	11.35	Referance	10.67
	SF-SFD	42.67	48.79	7.51	49.36	8.75	1.87	8.57
	CF-SFD	39.28	49.99	10.80	51.14	12.19	0.78	12.17
UNKNOWN (NAVY)	SF-CD	33.14	-6.34	-16.95	18.10	249.49	Referance	10.82
	SF-SFD	43.62	-7.67	-16.98	18.63	245.68	6.23	5.15
	CF-SFD	33.58	-6.59	-17.16	18.38	249.00	0.35	10.63
BLUE 21	SF-CD	63.90	-35.57	-29.40	46.15	219.57	Referance	13.69
	SF-SFD	73.53	-32.55	-22.50	39.57	214.65	3.21	6.04
	CF-SFD	59.76	-36.40	-27.69	45.74	217.26	4.08	18.61

SF-CD and CF-SFD trials were carried out in pilot scale trials by using %7 black dyestuff. The color strength (K/S) value for CF-SFD fabric was 20.3 while the SF-CD K/S value was 18.7 (see Table 5). This shows that 8.6% darker color was obtained with the cationization process. Arivithamani (2018) concluded in his study that the cationic fabric was 3% darker than the standard fabric in pilot trials. Besides, L, a, b values gives similar results as Black mix laboratory scale trials shown in Table 4. That means darkness and yellowness of CF-SFD fabric is higher than SF-CD fabric. Since ΔE value is higher than 1 point, it can be said that a significant positive result was taken with the cationization process.

3.2. Fastness results

Table 6 and 7 shows that washing, water, rubbing and light fastness results of the cationized and salt-free dyed cotton fabric were the same as untreated conventional dyed cotton fabric. While color staining values of acid and alkali perspiration fastness of the untreated fabric was 4/5, these values were 4 for the treated fabric and this value is still acceptable and good.

It can be seen from Table 8 that seam slippage and tear strength values were almost the same for both fabrics. However tensile strength of CF-SFD was similar to SF-CD. It shows that cationization process does not cause any strength loss.

3.3. Wastewater analysis results

Wastewater of all baths was analyzed in order to see the environmental effects of the salt-free dyeing process. Wastewater color of each bath for both conventional and salt–free dyeing was shown in Figure 6 and Figure 7. It was obviously seen that first neutralization bath after dyeing, first reactive washing bath and second reactive washing bath are clearer in salt–free dyeing process. Color measurements of wastewater were shown in Table 9. Wastewater of salt-free dyeing process has 34% - 69% lighter color. This means more dyestuff was exhausted by cationized fabric. This result was verified by K/S values of cationic fabric in Table 5. COD, conductivity and TDS values of all baths results were given in Table 10.

Table 5. Comparison of color strength of dyed fabrics in pilot-scale

PROCESS TYPE	L	a	b	C	h	ΔE	K/S
SF-CD	19.83	0.35	-3.07	3.09	276.54	Referance	18.7
CF-SFD	18.72	0.25	-2.03	2.05	276.90	1.56	20.30

Table 6. Fastness test results of dyed fabrics

FASTNESS TEST RESULTS	Washing ISO 105-C06:2012 A2@40ºC							Water ISO 105-E01:2013							Light Fastness	Rubbing Fastness ISO 105X12:2006	
PROCESS TYPE	CC	CA	CO	PA	PES	CA	WO	CC	CA	CO	PA	PES	CA	WO	ISO 105-B02	DRY	WET
SF-CD	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	3/4	4	3
CF-SFD	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	3/4	4	3

Table 7. Perspration fastness test results of dyed fabrics

FASTNESS TEST RESULTS	Acid Perspiration ISO 105-E04:2013							Alkali Perspiration ISO 105-E04:2013						
PROCESS TYPE	CC	CA	CO	PA	PES	CA	WO	CC	CA	CO	PA	PES	CA	WO
SF-CD	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
CF-SFD	4/5	4/5	4	4	4/5	4/5	4/5	4/5	4/5	4	4/5	4/5	4/5	4/5

Table 8. Strength test results of dyed fabrics

STRENGTH TEST RESULT	SEAM SLIPPAGE ISO 13936-2 (mm/60N)		TEAR STRENGTH ISO 13937-2 (Newton)		TENSILE STRENGTH ISO 13934-2 (Newton)	
PROCESS TYPE	WARP	WEFT	WARP	WEFT	WARP	WEFT
SF-CD	1	1	3.86	3.45	23.69	20.39
CF-SFD	1	1	4.36	3.70	18.11	20.33

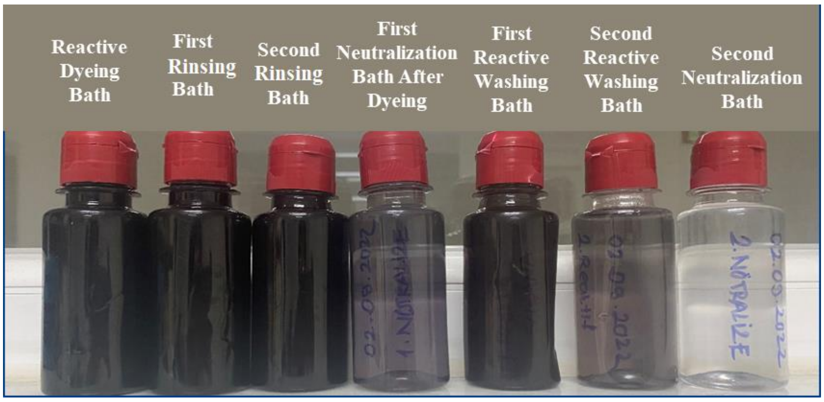

Figure 6. Conventional dyeing baths wastewater

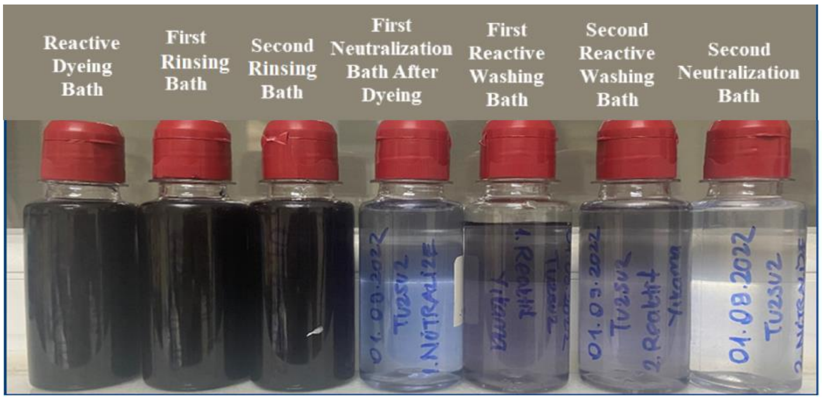

Figure 7. Salt - free dyeing baths wastewater

Table 9. Color measurements of wastewater for dyeing baths and washing baths after dyeing

BLACK DYEING PROCESS	COLOR (PtCo)	
	Conventional Dyeing	**Salt-Free Dyeing**
Reactive Dyeing Bath	>4500	>4500
First Rinsing Bath	>4500	>4500
Second Rinsing Bath	2446.00	1611.00
First Neutralization Bath After Dyeing	429.00	223.00
First Reactive Washing Bath	1423.00	443.00
Second Reactive Washing Bath	629.00	329.00
Second Neutralization Bath	41.00	25.00

Table 10. COD, conductivity and TDS values of all baths

BLACK DYEING PROCESS	COD (mg/L)		CONDUCTIVITY (ms/cm)		TDS (mg/L)	
	Conventional Dyeing	**Salt-Free Dyeing**	**Conventional Dyeing**	**Salt-Free Dyeing**	**Conventional Dyeing**	**Salt-Free Dyeing**
Cationization Bath	-	2218	-	31.80	-	≈9.94
Rinse Bath	-	1207	-	6.35	-	≈3.18
First Neutralization Bath	-	738	-	1.13	-	≈0.57
Reactive Dyeing Bath	2168	1565	64.80	17.44	≈38.88	≈9.94
First Rinsing Bath	528	373	9.65	3.16	≈4.83	≈1.58
Second Rinsing Bath	166	105	0.15	0.84	≈0.73	≈0.42
First Neutralization Bath After Dyeing	312	404	0.64	0.54	≈0.32	≈0.27
First Reactive Washing Bath	547	233	0.80	0.63	≈0.40	≈0.32
Second Reactive Washing Bath	147	197	0.53	0.57	≈0.26	≈0.29
Third Neutralization Bath	282	424	0.53	0.54	≈0.27	≈0.27

In terms of COD values, reactive dyeing bath of salt-free dyeing has lower COD value than conventional dyeing. On the other hand cationization bath causes extra waste load. Despite of this negative impact, conductivity and TDS results of salt-free dyeing were quite low when compared with conventional dyeing. As known, high total dissolved solids (TDS) causes difficulties on treatment and reuse of wastewater. TDS concentrations should be at a certain level for every type of water. High TDS concentrations in the presence of potassium, sodium, and chloride typically require a reverse osmosis system. Wastewater treatments by using reverse osmosis systems has high cost [6]. The conductivity values of wastewater change depending on the salt content. The higher salinity the less oxygen gets dissolved which may influence the bacteria at the biological treatment step. Another negative effect of high salinity might be corrosion of metals. Since all these undesirable effects will not be observed in the salt-free dyeing process, more environmentally friendly dyeing will be achieved.

4. CONCLUSIONS

In chemical optimization studies, it was observed that there was no significant difference in color strengths when using cationization agent over 50 g/L. In addition, when 50 g/L cationization agent was used, it has been determined that there was a serious decrease in color strength when using caustic below 17 g/L. When the trials were examined, lab-scale trials shows that the K/S values in salt-free dyeing process was changing depend on dyestuff types. The color strength of cationic dyed fabrics in all colors is greater than the color strength of conventional dyed fabrics. While almost no difference is in Navy, it is greatest in Blue 221 with 61%.

In pilot-scale trials, color strength of cationic dyed fabric is 8.6% higher than in conventional dyeing process. That means less dyestuffs will be used in salt-free dyeing to get same color. In a similar study in the literature, the amount of cationization agent is 80 g/L, while the color difference is 3%. In this study, it was observed that better results were obtained with 50 g/L [25].

Thus, the less dyestuff in the dyeing baths will reduce the color of wastewater. Apart from this, the total amount of dissolved solids in the waste water will decrease with the absence of salt in the dyeing processes. For this reason, there is no need for reverse osmosis systems for wastewater treatments. And biological treatment will be suitable while wastewater treatment. Also the novel process does not cause corrosion. Besides cationization process causes additional waste load depending on cationization bath. It was concluded that a darker color was obtained without compromising the strength and fastness values of the cationized fabric. Therefore, salt-free dyeing can be achieved by cationizing the fabrics with amino compounds before dyeing.

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