101 Egypt. J. Chem. Vol. 66, No. 3, pp. 1 - 19 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Treatment of Cotton Fabrics using Polyamines for Improved Coloration with Natural Dyes Extracted from Plant and Insect Sources

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Abstract

The color strength of the modified colored cotton fabric with polyethyleneimine (PEI) or chitosan using cochineal and moringa natural dyes was examined in this study. Polyethyleneimine and chitosan therapy have led to remarkable increases in cotton fabric dyeability according to colorimetric tests. The fabric treated with polyethyleneimine or chitosan was successfully dyed at lower temperatures in lower time than the untreated one. The change in the dyebath pH shows that the electrostatic force plays a significant role in color adsorption. The fastness properties, tensile strength, and elongation at a break of colored cotton were enhanced following treatment. The scanning electron microscopic (SEM) and Fourier Infra-Red FT-IR analysis proved that cotton fabric has been coated with a thin and consistent polyethyleneimine or chitosan layer, which enhanced cotton fabric coloration with moringa and cochineal dyes.

Keywords: Cotton; Moringa leaves extract; cochineal; polyamines polymer

1. Introduction

After the advent of synthetic dyes on the market in the mid-19th century, the employment of natural dyes in textile coloring has dropped dramatically. In recent years the interest in natural dyes has been rekindled due to legislative prohibitions on the use of some synthetic dyes with certain chemical structures, due to the rising ecological and environmental consciousness of people. **[1-3]**

In addition, the antibacterial and anti-fungal protective qualities of fabrics with certain natural dyes have been observed. **[4, 5]** While natural dyes are intended to be more environmentally friendly, they have problems with low exhaustion and fixation on textile materials. **[6]** In developing the natural dyeing processes, the poor affinity between most natural dyes and textile fiber is a major challenge. **[7]**

Metal mordants are the most frequent compounds used to improve the exhaustion, attachment, color strength, and fastness property of natural dyes onto different textile fibers such as cotton, silk, and wool. **[8-11]** However, they create effluent residual harmful metal ions that harm the environment and cause major health and allergy problems. **[6, 12-14]**

Several approaches have been investigated for the improvement of natural dyeing of natural fabric without metallic mordants such as ultrasonic power, **[15-21]** microwaves, **[22-27]** gamma, **[28-31]** UV, **[32]** enzymes, **[33-36]** plasma, **[37-43]** nano clay, **[44, 45]** and chitosan finish. **[46-52]**

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Receive Date: 09 May 2022, **Revise Date:** 13 June 2022, **Accept Date:** 26 June 2022, **First Publish Date:** 26 June 2022
DOI: 10.21608/EJCHEM.2022.137464.6053

A polyamine is an amino group that can take a positive acid charge and easily attaches to negative loaded surfaces and molecules, such as textile fibers and dyes. The use of anionic synthetic and natural dyes in acidic environments can be improved by polyamine. **[53-56]** Polyamines were regarded as a highly valuable and promising resource for use in a variety of applications, for example, food, cosmetics, biomedicine, and agricultural and chemical industries. **[57, 58]**

Natural clay is composed of silicon tetrahedral plates between aluminium octahedral plates and was one of the smectite groups of montmorillonite (MMT). The high negative charge of the imperfection of the crystal grid and isomorphic replacement leads to adsorption on alkaline earth metal ion interlayer spaces. [59]

As a result, both the pharmaceuticals and the active substance included the common ingredient MMT. [60] The intercalation of biodiversity into inorganic layered solids offers a valuable and simple technique for producing an organic-inorganic hybrid in a single substance that has the characteristics both of the inorganic host and the organic invited individual. [61]

Research over a day has demonstrated that Cochineal and Moringa Oleifera's leaves have strong naturally occurring good color, and antioxidant properties and are antibacterial to gram-positive and gram-negative bacteria. **[62-73]**

The goal of this study is to increase the dyeing uptake of natural dyes (moringa and cochineal) onto cotton fabrics using polyamine compounds (chitosan and polyethyleneimine) in combination with clay.

2. Experimental

2.1. Materials

Bleached cotton fabric (207 g/m^2) supplied by Misr El-Mehala Co. for Spinning and Weaving, Egypt. Low Molecular weight Chitosan 100000 – 300000 was supplied by Fluka. Hyperbranched polyethylenimine average molecular weight ~30000 have been purchased from Sigma – Aldrich. Montmorillonite (MMT - K10, Molecular Formula: $H_2Al_2(SiO_3)_4.n H_2O$) manufactured by ACROS Organics was used. *Moringa Oleifera* leaves were purchased from the local market in Egypt. Cochineal (Dactylopius coccus) was purchased from Canaturex, Spain. Ethanol (C_2H_5OH; 95%), acetic acid (CH_3COOH), sodium carbonate (Na_2CO_3), citric acid ($C_6H_8O_7$), sodium hypophosphite ($NaPO_2H_2$, SHP), and butane tetracarboxylic acid ($C_8H_{10}O_8$) were provided from Fluka. nonionic detergent (Hostabal NG) was supplied by Clarinet Co.

2.2. Methods

2.2.1. Preparation of Stock Solution of Natural Dyes

2.2.1.1. Preparation of Moringa Oleifera leaves extract

Extraction of *Moringa Oleifera* leaves was done according to our previous work. [47] In brief, 20 g dried *Moringa Oleifera* leaves were placed in 500 ml ethanol in the Soxhlet system at boiling temperature for 24 h. The ethanol extract was then concentrated using a rotary evaporator to 250 ml, and the extract was used without any purification. The chemical structure of dye in *Moringa Oleifera* leaves was illustrated in Figure 1.

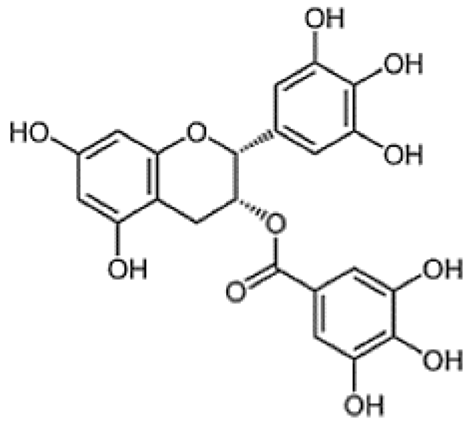

Figure 1: Chemical structure of dye in Moringa Oleifera leaves

2.2.1.2. Preparation of Cochineal dye

Cochineal dye was prepared according to the following procedure: In brief, 10 g dried Dactylopius coccus were grinded into a fine powder and dried in an oven at 70°C for 30 min., then placed in 1000 ml distilled water under stirring at room temperature for 1 h. The extract was used without any further purification. The chemical structure of *Cochineal* dye was illustrated in Figure 2.

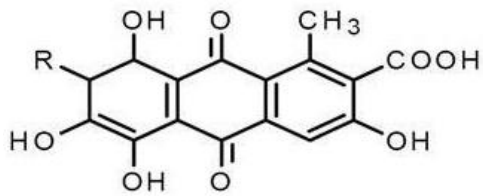

Figure 2: Chemical structure of dye in cochineal

2.2.2. Preparation of treatment formula based on chitosan polymer

Chitosan solutions with different concentrations (0.5, 1, 2, or 3 %w/v) have been prepared by dissolving chitosan powder in 2% acetic acid solution under continuous stirring. After complete dissolving, different amounts of clay (0.25, 0.5, 0.75, or 1% w/v) have been added to the prepared solutions under stirring for about 3h. After complete mixing of composite, the solutions have been undergoing ultrasonic radiation for about one h. Thus, obtained composites have been used to treat cotton fabrics**.**

2.2.3. Preparation of treatment formula based on hyperbranched Polyethyleneimine

Different amounts of polyethyleneimine polymer (0.5, 1, 2, or 3% w/v) have been dissolved in distilled water under stirring. After that different amounts of clay (0.25, 0.5, 0.75, or 1 % w/v) have been added to the prepared solutions under stirring undergoing for about 3h. After complete mixing of composite, the solutions have been to ultrasonic radiation for about one h. Thus, obtained composites have been used to treat cotton fabrics**.**

2.2.4. Treatment of cotton fabrics

Cotton fabric was pre-treated via pad dry technique with butane tetracarboxylic (BTCA; 10 g/L) acid and sodium hypophosphite (SHP; 5 g/l), with 80 % wet pickup and drying for 3 min at 100°C. After that, cotton fabrics have been immersed in the solutions of each previous composite for about 20 min. The samples were then padded to a wet pick-up of 100% followed by drying for 5 min at 100°C. Finally, the fabric samples were cured for 3 min at 140°C. The treated fabrics have been washed with a washing solution containing 2.5% non-ionic detergent to get rid of unreacted compounds.

2.2.5. Dyeing Procedure

Dyeing of the fabric samples was performed using both natural dyes (moringa, or cochineal). Dyeing parameters were studied such as: (i) pH (2, 3, 5, 7, and 9), (ii) temperature (50, 60, 70, 80, and 90°C), (iii) time (30, 60, 120, and 180 min.), and (iv) liquor ratio (1: 20, 1:30, and 1:50). the solution pH was adjusted using acetic acid or sodium carbonate. In the beginning, the fabric sample was placed in a dyeing bath at 40°C, then the temperature was raised to the final temperature of 2°C/min, and then continued for an examined time during this study. **[74-76]**Finally, the samples were rinsed with tap water and dried at ambient temperature.

2.3. Measurements

2.3.1. Color Strength Measurement

The color strength of the dyed treated cotton fabrics with both natural dyes was measured by the Hunter Lab Ultra-Scan Pro at the National Research Centre in Egypt and is represented as K/S. The K/S values were determined using the Kubelka–Munk equation: **[77-81]**

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

where K is the coefficient of absorption, S is the coefficient of dispersion, and R_{kmax} is the reflectance of the cloth at its maximum wavelength.

2.3.2. Determination of the amine content

Amine content of the prepared materials and/or fabrics according to the following method: weight about 0.25 g of the sample and put it a 250 ml stoppered conical flask, the 40 ml of 0.1 N HCl (30 g NaCl + 10 g HCl in one liter, then standardized with $Na_2S_2O_3$) was added. The conical flasks were left overnight with occasional shaking. Filter, then titrate the filtrate against NaOH (0.05 N) with phenolphthalein as an indicator. Amino content percent was calculated according to the following equation:

$$\text{amine contents \%} = \frac{(V_B - V_S) \times M_{NaOH}}{W_t} \times 100$$

which V_b is the Volume of NaOH consumed by blank experimented, V_s is the Volume of NaOH consumed by the sample, M_{NaOH} = Molarity of NaOH, and W is the weight of the sample in H form.

2.3.3. Colorfastness properties

The colorfastness to washing was determined using a Launder-Ometer following the AATCC test method 61-2013. **[82]** The colorfastness to rubbing (dry and wet) was determined using a Crockmeter following the AATCC test method 8-2016. **[83]** The colorfastness to perspiration (acid and alkaline) was determined by following the AATCC test method 15-2013. **[84]** The colorfastness to light was determined according to the AATCC test method 15-2013. **[85]** the grayscale reference for the color shift was used to evaluate washing, rubbing, and perspiration fastness properties, while the blue scale reference for color change was used to evaluate the light fastness property for dyed fabrics.

2.3.4. Relative Unlevelness Index (RUI)

Reflectance values (R) of ten-point on each dyed fabric sample were measured using a reflectance spectrophotometer in the visible spectrum range. The relative unleveled index (RUI) was calculated according to the following equation

$$\mathrm{RUI} = \sum_{\lambda=390}^{\lambda=700} (S_\lambda/R_a)V_\lambda \quad \text{and}$$

$$S_\lambda = \sqrt{\frac{\sum_{i=1}^{n}(R_i - R_a)^2}{n-1}}$$

where S_λ is the standard deviation, R_a is the average of reflectance values of n measurements for each wavelength and V_λ is the photopic relative luminous efficiency function. R_i is the reflectance value of the measurement number (i) for each wavelength. RUI value can be explaining the levelness behavior according to the following classification: **[86-89]**

- If RUI < 0.2, so, it was considered as excellent levelness,
- If 0.2 < RUI < 0.49, it was considered as good levelness,
- If 0.5 < RUI < 1, means poor levelness, and
- RUI > 1, indicate bad levelness

2.3.5. Dye Fixation Measurement

Dyed fabrics were washed at 50°C for 30 min to test the dye fixation. The color strength values of the colored fabric after and before washing have been determined. The following equation was used to determine the dye fixation (%F)

$$\% \mathrm{F} = \frac{(K/S)_a}{(K/S)_b} \times 100$$

where $(K/S)_a$ is the color strength of the dyed fabric after washing and $(K/S)_b$ is the color strength of the dyed fabric before washing.

2.3.6. Scanning Electron Microscopy (SEM)

The surface morphology was examined by Scanning Electron Microscopy (SEM/EDX) HITASHI S–3000 microscope S.

2.3.7. Transmission Electron Microscopy (TEM)

The particle's behavior of the prepared treatment solution with both polyamines was examined using Transmission Electron Microscopy (TEM) JEOL JEM-1200 EX at 120 KV. TEM measurements were prepared by dissolving a drop of colloid solution on a 400-mesh copper grid coated with an amorphous carbon film and evaporating the solvent in the air at room temperature.

2.3.8. Particle Size Analyser (PSA)

The particle size of the prepared treatment solution with both polyamines in the presence and absence of clay was examined and characterized by laser particle size analyzer MasterSizer/2000 (MALVERN Instruments, UK) according to ASTM ، E11:61 **[90]** and BS 410-1 and 2: 2000, **[91, 92]** ISO 565: 1990. **[93]**

2.3.9. ATR-FTIR Analysis

FT-IR spectra were studied using a JASCO FT-IR spectrophotometer in the region of 4000-400 cm^{-1} with an ATR unit

2.3.10. Antimicrobial Measurement

Nutrient agar broth media was prepared with pH 7.4 ± 0.2 according to the following recipe:

Yeast extract 2.0 g/L
Peptone 5.0 g/L
Meat extract 1.0 g/L
NaCl 5.0 g/L

Prepared media was stored below 8°C, protected from direct light. Store dehydrated powder, in a dry place, in tightly sealed containers at 2-25°C.

Bacteria used in this study were gram-negative bacteria: *Escherichia coli* (ATCC 25922), gram-positive bacteria: *Staphylococcus aureus* (ATCC 6538), and pathogenic yeast: *Candida* albicans (ATCC 10231). The inoculation of all microorganisms was prepared from fresh overnight broth cultures that were incubated at 37°C. **[94]**

The inoculum size of these pathogenic strains was prepared and adjusted to approximately 0.5 McFarland standard (1.5×10^8 CFU/mL), 25 µL of both bacterial & yeast suspensions were inoculated into each plate containing 20 mL of the sterile nutrient medium (NA).

The samples were applied to these tested microorganisms by using the shake flask method to calculate the antimicrobial activity throughout (%) reduction of the growth of these selected pathogenic strains was detected by optical density (OD) at 600.0 nm and the antimicrobial activity was measured throughout the relative [OD (%)] reduction of these pathogenic strains after treated with the textile disc samples compared to the control of these pathogenic strains have no any treatment. **[95-98]**

All results were expressed according to the following equation:

$$Relative\ \big(OD\ Reduction\ (\%)\big) = \frac{A - B}{A} \times 100$$

where A: the (OD) of the control flask contains pathogenic strains only without any treatment, B: the (OD) of tested flasks after applying a disc sample treated.

3. Results and Discussion

3.1. Characterization of the treatment materials

Four different treatment solutions based on polyamine compounds have been prepared to functionalize the surface of cotton fabric. Polyethyleneimine and chitosan with different concentrations (0.5, 1, 2, and 3 %) with/without clay have been prepared and characterized for their particle size using a particle size analyzer and transmission electron microscope. The analysis provides that, the final prepared materials are in good distribution form and the clay particles are distributed well in the polyamine network which is shown in the TEM image in Figure 3 (A-D). These findings are in the same line with particle size analysis and provide a similar particle size to the TEM image.

These composites were examined using a particle size analyzer and the findings are displayed in Figure 4. The preparation of composites that contain polyethyleneimine or chitosan in presence of clay was bigger than those which contain polyethyleneimine or chitosan only, possibly because of a chemical combination of polyamine and clay components.

Figure 3 illustrates TEM pictures of the produced solution of polyethylene or chitosan in the presence or absence of clay. Figure 3 also illustrates the dispersion of clay in the polymer was in spherically formed particles. It was obvious from TEM pictures that the matrix included small spherical clay. Composites also exhibit an excellent dispersion across their network of clay particles.

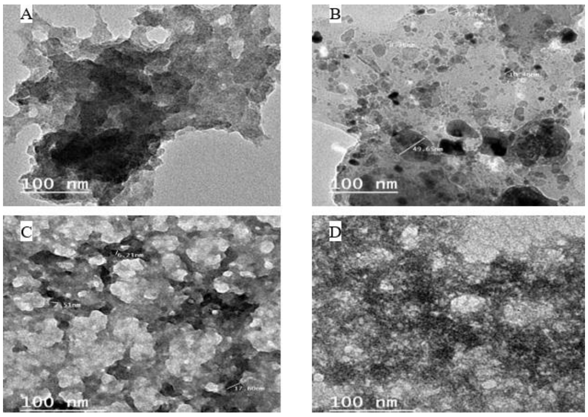

Figure 3: TEM images for prepared treatment solution with/without clay
A) Chitosan, B) Chitosan/clay
C) PEI D) PEI/Clay

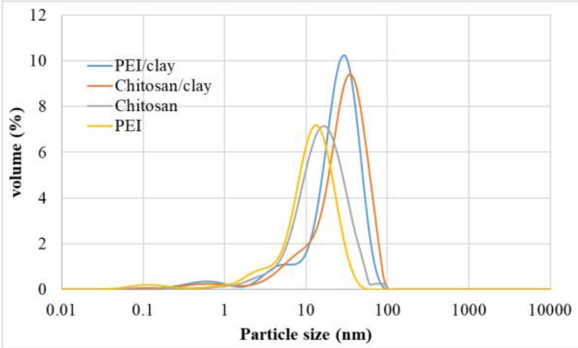

Figure 4: particle size analysis for prepared treatment solution with/without clay

3.2. Optimization of the modification parameters

3.2.1. Effect of polyamines concentration

Table 1, Figure 5**,** and Figure 6 represent the amine content and color strength (K/S) values dyed pre-treated fabrics with different concentrations (0.5, 1, 2, and 3 %) of polyamine content namely (chitosan, polyethyleneimine in the presence and absence of clay(clay (0.5 %))) using natural extracted dyes from both moringa and Cochineal (at pH 7, LR 1:30 for 60 min, at 70°C for moringa and 100°C for Cochineal).

Amine content for pre-treated fabrics provides increasing in amine content upon increasing the polyamine concentration in the pre-treatment process, which led to an increase in the color strength of the dyed fabric with both moringa and Cochineal compared to the untreated cotton fabric. Furthermore, pre-treated fabric with PEI provides higher amine content and relatively K/S values than pre-treated fabric with chitosan for all studied concentrations.

In addition, adding clay to both chitosan and PEI in the pre-treatment process led to improvement in the K/S values of dyed fabric with both examined dyes. While the amine content was deceased due to the chelation of metals in clay with the hydrogen of a primary amine in both chitosan and PEI.

Rather than, in presence of clay, decreasing in amine content is observed, and enhancement in K/S values was also observed. this observation is due to the presence of different metal cations in the composition of clay which improves the absorption of dye molecules into the fabric.

The important observation is increasing the concentration of polyamine in the pre-treatment process by more than 2 percent provides a slight enhancement in K/S values of dyed fabrics which led to conclude that, the pre-treatment of the fabrics with a 2% polyamine compound is more suitable for this investigation.

Table 1: amine content and color strength (K/S) values for dyed pre-treated fabrics with different polyamines types and concentrations

Polyamines		NH2 (mg/1 g fabric)	NH2 (%)	K/S	
				Moringa (415 nm)	Cochineal (525 nm)
Untreated fabric			1.11	0.98	0.9
Polyethyleneimine (PEI)	0.5	315.21	21.65	6.38	8.89
	1	371.30	43.30	6.47	10.07
	2	390.00	50.52	7.77	12.65
	3	408.70	57.73	8.31	15.63
Polyethyleneimine (PEI)/Clay	0.5	352.60	36.08	9.14	10.07
	1	361.95	39.69	9.27	11.9
	2	399.35	54.12	10.82	12.76
	3	483.49	86.60	12.41	13.13
Chitosan	0.5	268.46	3.61	2.81	1.78
	1	277.81	7.22	2.52	2.17
	2	305.86	18.04	4.72	6.34
	3	324.55	25.26	4.9	6.79
Chitosan/Clay	0.5	305.86	18.04	6.94	5.8
	1	324.55	25.26	8.61	7.34
	2	333.90	28.87	9.85	10.16
	3	343.25	32.47	10.57	11.87

Butantetracarboxylic acid (10 g/L); sodium hypophosphite (5 g/L); Polyamines (X %); clay (0.5 %)

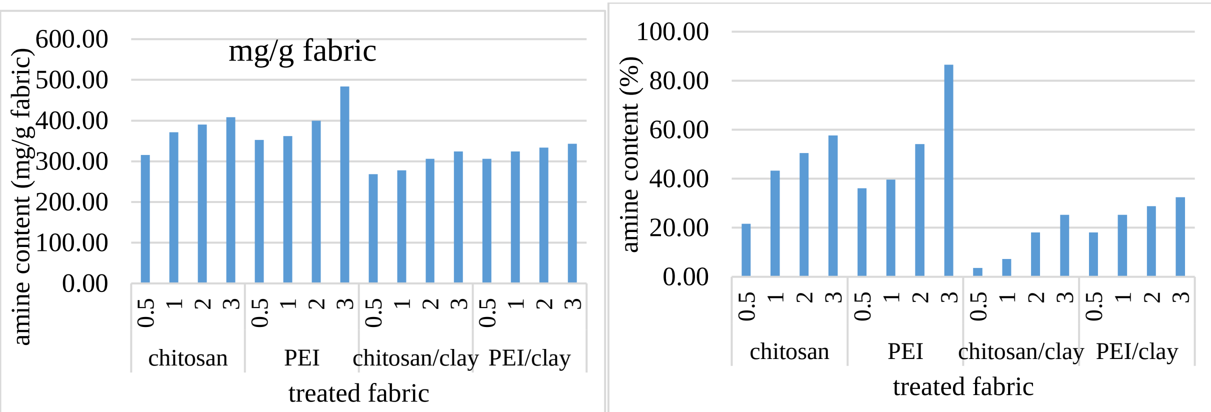

Figure 5: amine content for pre-treated fabrics with different polyamines types and concentrations

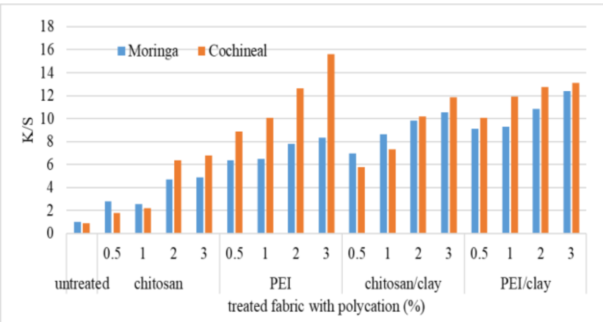

Figure 6: color strength (K/S) values for dyed pre-treated fabrics with different polyamines types and

concentrations

3.2.2. Effect of clay concentration

Table 2 and Figure 7 represent the color strength (K/S) values for dyed pre-treated fabrics with 2% polyamine content namely (chitosan, polyethyleneimine in presence of different concentrations of clay (0.25, 0.5, 0.75, and 1 %)) using natural extracted dyes from both moringa and Cochineal.

Table 2: color strength (K/S) values for dyed pre-treated fabrics with 2% polyamine and different clay concentration

Polyamines (2%)	Clay conc. (%)	K/S	
		Moringa (415 nm)	Cochineal (525 nm)
Untreated fabric		0.98	0.9
Polyethyleneimine (PEI)/clay	0.25	7.65	9.84
	0.5	9.14	10.07
	0.75	9.50	10.94
	1	9.54	11.12
Chitosan/Clay	0.25	6.65	5.02
	0.5	6.94	5.80
	0.75	6.85	6.20
	1	6.84	6.53

Butantetracarboxylic acid (10 g/L); sodium hypophosphite (5 g/L); Polyamines (2%); clay (x %)
Dyeing condition:

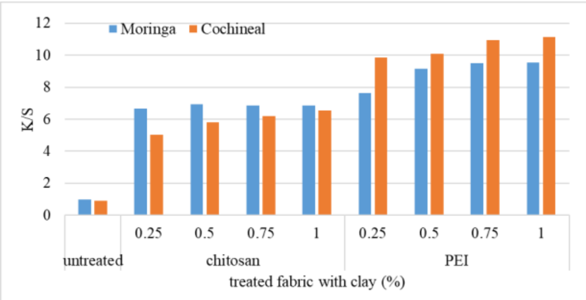

Figure 7: color strength (K/S) values for dyed pre-treated fabrics with 2% polyamine and different clay concentration

3.3. Optimization of the dyeing conditions

3.3.1. Effect of Dyeing pH medium on Color Strength

Table 3 shows the color strength (K/S) values for the dyed treated cotton fabrics with a polyamine in the presence and absence of clay using moringa and cochineal extract at different pH. The color strength of cotton fabrics modified by polyamine (PEI and chitosan) in the presence or absence of clay provide increasing the K/S values as the dyeing pH increases from pH 2 to pH 7, after that increasing the pH medium to alkaline (pH 9) causing decreasing the K/S values for all treated fabrics. Furthermore, treated fabric with PEI provides higher K/S values than treated fabric with chitosan which is due to the higher amount of nitrogen content which increases the absorption of dye to the fabric.

In addition, the presence of clay in treatment formulation causes increases in the K/S values of dyed cotton fabrics with both investigated natural dye more than polyamine only, this may be as a result of the presence of different metals in the clay components which play a role in the absorption of more dyes molecules.

PEI and chitosan incorporate amino groups in their chemical composition which can then protonate into an acidic solution and then form ionic bonds with anionic dyes which is the main colorant in cochineal and moringa. Carminic acid is the cochineal's primary colorant and has one carboxylic group and eight hydroxyl groups in its chemical structure which causes the formation of an anionic charge in the dyeing bath and then increases the ability of the fabric (carrying cationic charge) to adsorb the dye (anionic charge). The anionic load of carminic acid in water caused substantiate positively charged amino groups in polyamine on modified cotton fabric.

As the positive charge of amino groups of polycation in higher pH values (pH 9) declines, anionic dyes can be absorbed and causing a reduction in color strength (K/S). This process has the same effect on the absorption in both moringa and cochineal as anionic dyes.

3.3.2. Effect of Dyeing Temperature on Color Strength

Table 4 presents the color strength (K/S) values for the dyed treated cotton fabrics with a polyamine in the presence and absence of clay using moringa and cochineal extract at different dyeing temperatures (50, 60, and 70°C for moringa and 50, 60, 70, 80, 90 and 100°C for cochineal). The color strength of cotton fabrics provides increasing in the K/S values as the dyeing temperature increases from 50 to 70°C for moringa and from 50 to 100°C for cochineal. This is that the use of higher temperatures leads to increasing in fiber swelling and destroying the aggregation of the dye molecule, which consequently enhances the dye diffusion into the modified cotton fabric. **[10, 99, 100]**

3.3.1. Effect *of Dyeing Time on Color Strength*

The color intensity of dyed treated cotton fabrics with both natural dyes has grown as the dyeing temperature increases from 30 to 120 minutes, as illustrated in Table 5

. Then, as the dying time increased to 180 minutes, the color intensity decreased. It appears that after 120 minutes, the dyeing process has attained equilibrium. Heating disrupts the equilibrium over a long time, which leads to decreased K/S value. **[3]** This decrease may also be attributed to the partial degradation of the natural dye molecules due to prolonged exposure to high temperatures. **[99]**

3.3.1. Effect of Dyeing liquor ratio on Color Strength

As shown in Table 6 changes in the liquor ratio cause changes in color intensity of dyed treated cotton fabrics using both natural dyes. It is clear from the listed K/S values that, the 1: 20 liquor ratio is the best one with the highest value than the other two examined ratios for all treated fabrics. This phenomenon could be attributed to the good distribution and accumulation of dyes particle in the dyeing bath which provides good penetration of extra dye molecules inside the fabric leading to increasing the K/S.

3.4. Characterization of the dyed fabrics

3.4.1. ATR-FTIR Analysis

The ATR-FTIR spectrum for the treated cotton fabrics is shown in **Figure 8**. The peak at 1650 cm^{-1} is related to the amino groups of the polyamine chain. After modification of cotton fabric using polyamine compounds in the presence or absence of clay, a shoulder peak appeared at 1727 cm^{-1} which could confirm the formation of new amide groups between amine groups of polyamine and carboxyl groups of crosslinker.

The FTIR spectra for treated fabric with each polyamine were presented in **Figure 8** demands for NH_2 groups to be present in 3000-3200 and 1590 cm^{-1} absorption bands. It is found a stretch peak in the wavelength of 1240 cm-1 which is related to C-O from phenol or alcohol. **[101]**

The FTIR spectra have high wavelengths between 1650 and 1670 cm^{-1} of the ester or amide group. Furthermore, the IR spectral findings for the presence of clay during the coating process have been shown to associate polyamines with crosslinker and clay molecules. The metals in clay cause the hydrogen bonding of chitosan with a combination of surface and clay to be restricted. **[101]**

Table 3: color strength (K/S) values for the dyed treated cotton fabrics with a polyamine in the presence and absence of clay using moringa and cochineal extract at different pH

Polyamines	pH	Moringa (415 nm)				Cochineal (525 nm)			
		K/S	L*	a*	b*	K/S	L*	a*	b*
Polyethyleneimine (PEI)	2	5.51	58.37	2.89	21.08	0.84	64.45	9.60	5.45
	3	7.58	62.49	3.07	30.09	4.20	44.90	26.23	-0.60
	5	6.96	64.88	1.24	29.73	5.27	41.20	24.52	-4.62
	7	17.87	54.77	2.68	36.49	9.21	37.65	28.42	-6.18
	9	15.27	59.27	2.05	37.20	7.14	38.22	32.19	-5.53
Polyethyleneimine (PEI)/Clay	2	3.64	68.71	0.68	27.66	1.41	59.64	18.72	4.66
	3	6.87	62.62	2.53	31.86	2.21	53.52	23.37	-0.72
	5	6.89	62.04	2.80	29.16	8.54	37.25	33.49	-3.07
	7	18.85	60.68	3.70	45.54	10.30	36.35	36.31	-2.98
	9	14.96	62.01	2.14	46.57	7.37	39.41	34.94	-4.32
Chitosan	2	2.02	78.04	-2.35	14.16	0.83	67.52	13.25	8.76
	3	2.89	74.95	-2.64	17.83	1.44	59.25	17.34	3.87
	5	3.98	69.60	0.83	21.54	3.42	48.32	24.62	-3.35
	7	4.27	71.82	-1.03	22.60	3.72	64.26	15.34	-3.03
	9	3.90	69.25	0.26	24.67	0.93	47.41	25.28	-3.29
Chitosan/Clay	2	2.21	73.81	-1.78	18.73	0.92	65.53	15.52	6.41
	3	3.24	73.15	-2.78	22.25	1.80	54.61	19.72	3.72
	5	3.58	70.61	-2.71	24.25	2.05	46.84	27.84	-3.17
	7	9.73	56.02	2.13	33.09	6.25	58.65	28.47	-1.55
	9	6.19	64.54	-0.87	35.72	0.73	67.98	16.32	-1.81

Treatment condition: Butantetracarboxylic acid (10 g/L); sodium hypophosphite (5 g/L); Polyamines (2 %); clay (0.5 %), Dyeing condition: dyeing time 30 min.; dyeing Temp. 100°C; L.R 1:30; different pH

Table 4: color strength (K/S) values for the dyed treated cotton fabrics with a polyamine in the presence and absence of clay using moringa and cochineal extract at different dyeing Temperature

Polyamines	Temp.	Moringa (415 nm)				Cochineal (525 nm)			
		K/S	L*	a*	b*	K/S	L*	a*	b*
Polyethyleneimine (PEI)	50	9.91	65.45	1.36	36.29	5.30	41.80	29.44	-5.96
	60	10.15	65.18	1.40	37.21	7.55	37.84	31.50	-5.61
	70	17.87	54.77	2.68	36.49	5.18	40.29	24.38	-7.04
	80	--	--	--	--	6.83	36.81	25.43	-5.93
	90	--	--	--	--	5.46	39.18	22.88	-6.33
	100	--	--	--	--	9.21	37.65	28.42	-6.18
Polyethyleneimine (PEI)/Clay	50	11.66	63.15	3.06	42.50	8.45	38.25	36.80	-3.21
	60	12.24	63.69	2.65	39.53	8.43	37.80	35.20	-3.51
	70	15.85	60.68	3.70	45.54	6.00	40.79	31.06	-4.23
	80	--	--	--	--	7.70	38.29	33.54	-4.83
	90	--	--	--	--	8.95	35.89	32.49	-4.68
	100	--	--	--	--	10.30	36.35	36.31	-2.98
Chitosan	50	4.43	70.56	0.91	20.51	4.90	43.98	28.02	-3.10
	60	4.27	71.82	-1.03	22.60	7.16	39.39	29.29	-3.06
	70	5.72	76.76	-1.75	16.05	2.61	49.58	16.78	-1.14
	80	--	--	--	--	3.78	44.37	18.86	-1.91
	90	--	--	--	--	2.04	52.20	14.02	-3.47
	100	--	--	--	--	3.72	64.26	15.34	-3.03
Chitosan/Clay	50	1.86	76.80	-0.97	14.05	4.57	45.22	29.65	4.57
	60	9.73	56.02	2.13	33.09	5.14	43.72	29.36	5.14
	70	10.90	77.30	-1.24	13.96	6.09	38.57	22.95	6.09
	80	--	--	--	--	3.20	47.60	21.29	3.20
	90	--	--	--	--	3.27	47.73	22.87	3.27
	100	--	--	--	--	6.25	58.65	28.47	-1.55

Treatment condition: Butantetracarboxylic acid (10 g/L); sodium hypophosphite (5 g/L); Polyamines (2 %); clay (0.5 %), Dyeing condition: dyeing time 30 min.; dyeing Temp. X°C; L.R 1:30; pH 7

Table 5: color strength (K/S) values for the dyed treated cotton fabrics with a polyamine in the presence and absence of clay using moringa and cochineal extract at different dyeing times

Polyamines	Time (min.).	Moringa (415 nm)				Cochineal (525 nm)			
		K/S	L*	a*	b*	K/S	L*	a*	b*
Polyethyleneimine (PEI)	30	15.21	59.54	0.88	35.18	11.69	32.07	30.44	-4.22
	60	17.87	54.77	2.68	36.49	7.46	36.66	25.75	-4.06
	120	22.80	55.34	2.20	43.78	7.32	35.52	22.86	-3.81
	180	18.27	55.72	1.26	37.08	7.31	35.53	22.80	-3.64
Polyethyleneimine (PEI)/Clay	30	18.28	58.80	1.82	44.31	10.30	36.35	36.31	-2.98
	60	18.28	56.22	0.55	36.96	12.14	32.42	32.11	-2.37
	120	22.75	55.04	2.22	43.61	9.25	35.06	30.57	-4.99
	180	22.39	56.14	2.02	42.51	8.53	35.94	29.93	-5.05
Chitosan	30	9.67	63.31	-0.98	28.80	3.72	64.26	15.34	-3.03
	60	5.72	76.76	-1.75	16.05	6.96	53.99	11.74	-0.77
	120	12.87	57.10	-0.07	29.61	6.91	53.29	14.30	-0.73
	180	7.44	63.71	-1.80	26.35	4.96	53.30	14.34	-0.74
Chitosan/Clay	30	5.16	69.06	-2.02	25.18	6.25	58.65	28.47	-1.55
	60	10.90	77.30	-1.24	13.96	8.40	48.01	24.01	-2.18
	120	11.90	65.40	-1.42	25.79	6.19	48.11	21.03	-1.06
	180	10.01	60.37	-1.82	28.94	2.99	48.84	20.38	-0.61

Treatment condition: Butantetracarboxylic acid (10 g/L); sodium hypophosphite (5 g/L); Polyamines (2 %); clay (0.5 %), Dyeing condition: dyeing time X min.; dyeing Temp. 70°C; L.R 1:30; pH 7

Table 6: color strength (K/S) values for the dyed treated cotton fabrics with a polyamine in the presence and absence of clay using moringa and cochineal extract at different liquors ratio

Polyamines	LR	Moringa (415 nm)				Cochineal (525 nm)			
		K/S	L*	a*	b*	K/S	L*	a*	b*
Polyethyleneimine (PEI)	1:50	11.25	50.67	1.92	33.53	5.41	32.68	30.91	-4.22
	1:30	22.80	55.34	2.20	43.78	11.69	32.07	30.44	-4.22
	1:20	22.92	60.01	2.93	30.87	12.95	32.76	32.41	-4.39
Polyethyleneimine (PEI)/Clay	1:50	13.21	50.76	2.02	55.09	5.93	33.33	33.29	-1.78
	1:30	22.75	55.04	2.22	43.61	12.14	32.42	32.11	-2.37
	1:20	23.01	52.01	3.98	45.97	13.84	34.34	34.50	-2.78
Chitosan	1:50	9.45	50.10	-0.21	32.41	3.02	50.78	11.34	-0.71
	1:30	12.87	57.10	-0.07	29.61	6.96	53.99	11.74	-0.77
	1:20	14.84	40.91	-1.09	30.79	7.69	54.55	12.46	-0.87
Chitosan/Clay	1:50	10.20	61.09	-2.54	22.35	4.42	48.00	23.90	-2.21
	1:30	11.90	65.40	-1.42	25.79	8.40	48.01	24.01	-2.18
	1:20	13.65	64.00	-1.67	33.21	11.56	50.19	26.34	-3.82

Treatment condition: Butantetracarboxylic acid (10 g/L); sodium hypophosphite (5 g/L); Polyamines (2 %); clay (0.5 %), Dyeing condition: dyeing time 120 min.; dyeing Temp. 70°C; L.R X; pH 7

The amplitude of waves at 1670 and 1610 cm^{-1} was increased due to pre-treated cotton fabric with butane tetracarboxylic acid, which was the region for the C=O group.

Figure 9 shows the proposed mechanism for the reaction between polyamines and cotton fabrics. This image depicts the bonding method of polyamines via hydrogen or amide bonds to the pre-treated cotton surface with BTCA.

3.4.2. Surface morphology

Scanning electron microscopy (SEM) and transition electron microscope (TEM) were utilized to assess the morphological changes in cotton fabrics with various composites before and after dyeing with both nature dyes, and the images were in **Figure 10**.

SEM images for treated fabrics showed clearly that, the surface confirms the presence of a fairly rough morphology, and holes on the cotton fabrics surface are filled after composite treatment, as a result of coating with a homogeneous thin polyamine layer which causes decreasing in roughness property.

The following underlines another important observation. fabrics dyed with Moringa Olivera leaves ethanol extract to have a good dispersion in the cotton compound as fabrics dyed with cochineal in water without agglomeration. The addition of clay in composite formulation exhibits some agglomeration with excellent dispersion of clay on the fabric surface.

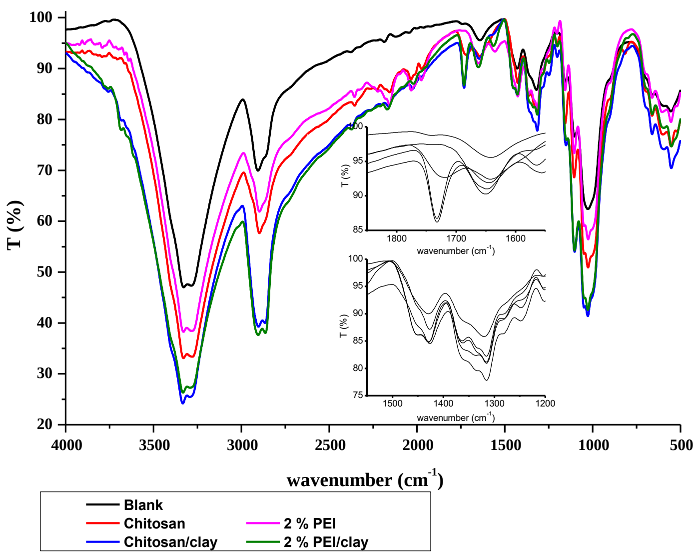

Figure 8: FT-IR spectra for treated fabrics with different composites

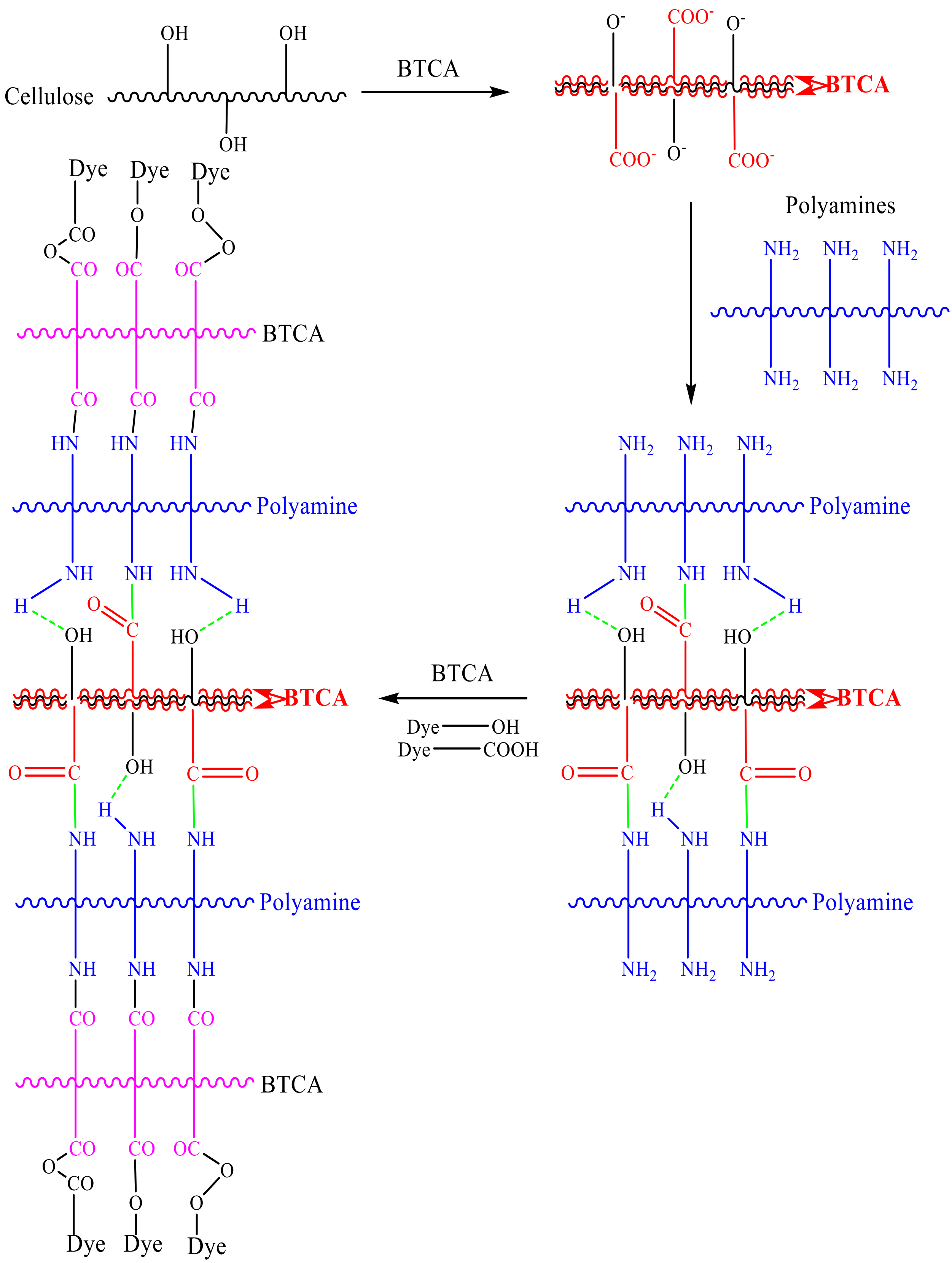

Figure 9: Proposed mechanism for the reaction between polyamines cotton fabrics and dye molecules

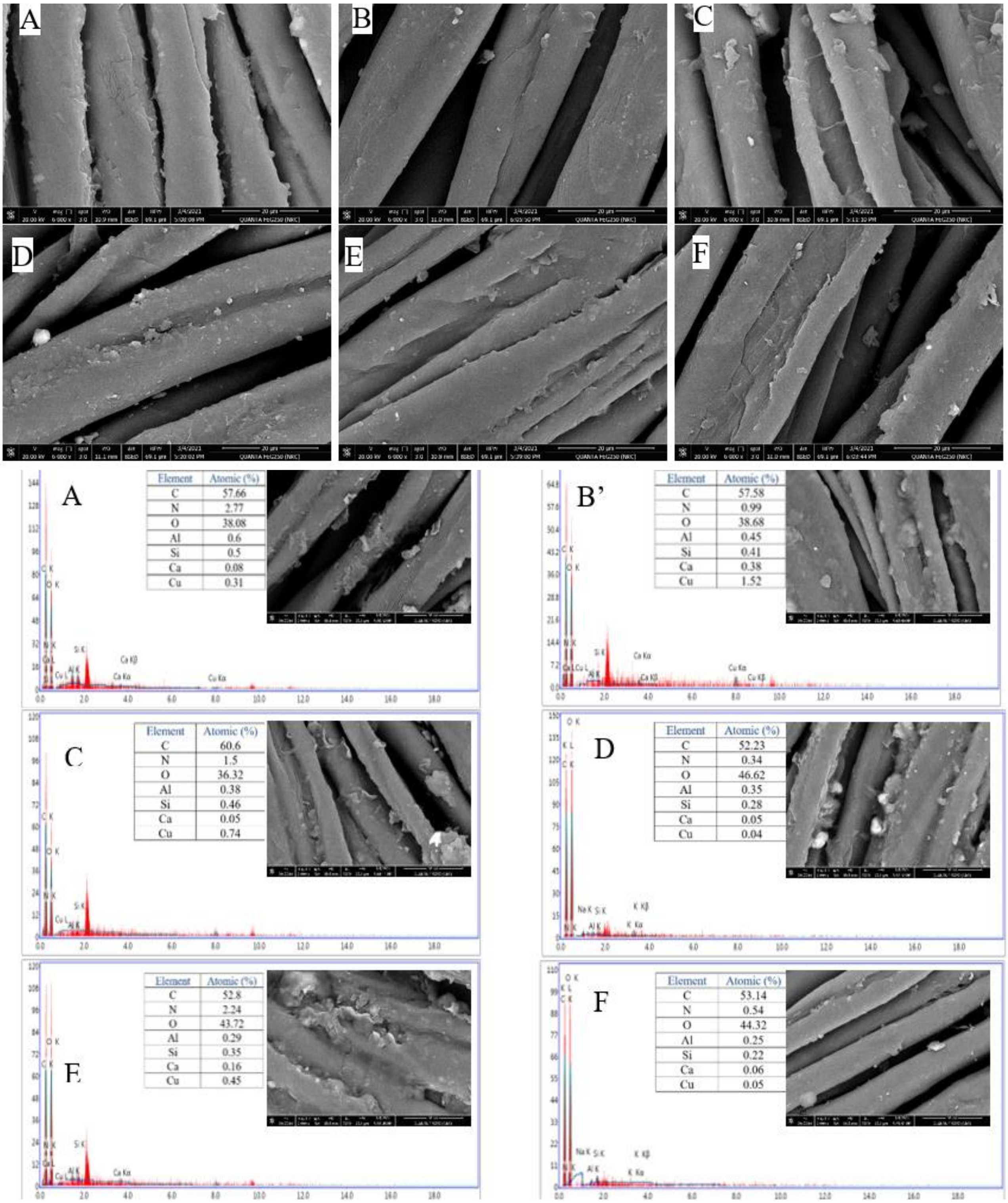

Figure 10: SEM and EDX images for treated cotton fabrics with different polyamine/clay and dyed with moringa and cochineal natural dyes

A, A') treated fabric with PEI and PEI/clay B, B') treated fabric with chitosan and chitosan/clay

C, C') treated fabric with PEI and PEI/clay dyed with moringa

D, D') treated fabric with chitosan and chitosan/clay dyed with moringa

E, E') treated fabric with PEI and PEI/clay dyed with cochineal

F, F') treated fabric with chitosan and chitosan/clay dyed with cochineal

3.4.3. *Especially remarkable was the fact that the picture of an EDX strongly shows the presence of certain metals on the surface of cotton when treated with clay and also after dyeing with both natural dyes.*

3.4.4. Coloring performance

Color strength, fastness properties, dye fixation, and relative unleveled index (RUI) for the dyed treated cotton fabrics with a polyamine (2 %) in the presence and absence of clay (0.5 %) using moringa and cochineal extract at optimum dying conditions (120 min.; 70°C; L.R 1:50; pH 7) were shown in

Table 7

In comparison with untreated fabric, treated fabrics demonstrated superior washing, perspiration, lighting, and rubbing fastness characteristics. Chitosan and polyethyleneimine treatment have significantly enhanced the washing and light fastness characteristics with dyed fabric using cochineal more than moringa. in contrast to the untreated cotton fabric, the polyamine treated fabric absorbs more dye molecules. The chemical bonds between modified cotton fabrics and dye modules are responsible for this improvement.

In addition, the presence of clay molecules in the polyamine network enhances the overall fastness properties of dyed fabric with both natural dyes. This could be attributed to increasing the hydrogen bonding between dye molecules, polyamine, cotton surface, and crosslinker, which the responsible for the fixation of the dye molecules inside and on the cotton surface.

The relative unleveled index (RUI) in

Table 7 demonstrates that when the fabric is treated with a polyamine in the presence or absence of clay, the level of dyeing has been enhanced from good to excellent. Those changes have enhanced the degree of dyeing because the cotton fiber has a thin film from polyamine compounds uniformly on the surface, and the dye molecules have been absorbed better and more uniformly.

The dye fixation of dyed untreated and treated fabrics was calculated according to the equation presented in the experimental part. As observed in

Table 7, treatment with polyamine compound in the presence or absence of clay improved the dye fixation of both natural dyes on cotton fabrics. This increase was higher for the fabrics treated with PEI than those treated with chitosan. Using both polyamines, the chemical interactions between the amino groups from polyamine compounds and hydroxyl groups in cotton surface or carboxyl groups from crosslinker and dye molecules caused a significant improvement in dye fixation.

3.4.5. Antimicrobial activity

Quantitatively examination using three types of microorganisms (gram-positive (Staphylococcus aureus), gram-negatory (Escherichia coli), or fungal bacteria (Candida Albicans)) were used to demonstrate antibacterial actions of the treated and dyed cotton fabrics with/without clay.

Table 7: color strength, fastness properties, dye fixation, and relative unleveled index (RUI) for the dyed treated cotton fabrics with a polyamine in the presence and absence of clay using moringa and cochineal extract at the optimum dying condition

Treatment	K/S		Fastness properties											RUI	% F
	Before washing	After washing	Washing		Rubbing				Perspiration				Light		
					Dry		Wet		Acidic		Alkaline				
			Alt	St	Alt	St	Alt	St	Alt	St	Alt	St			
Moringa															
Blank	8.24	3.26	2	2	2	2	2	2	2	2	2	2	2-3	0.41	39.56
Chitosan	17.09	14.84	2-3	2-3	2-3	2-3	2	2	2	2-3	2-3	3	3	0.25	86.83
Chitosan/Clay	16.01	13.65	3	3	3	3	3	3	3	3	3	3	3-4	0.23	85.26
PEI	24.21	22.92	3	3	3	3	3	3	3	3	3	3	4	0.21	94.67
PEI/Clay	24.35	23.01	3-4	3	3	3-4	3-4	3	3	3	3	3	4	0.19	94.50
Cochineal															
Blank	3.15	1.24	2	2	2	2	2-3	2-3	2	2	2	2	3-4	0.47	39.37
Chitosan	9.94	7.69	3	3	4	4-5	3	3-4	3	3-4	3	3	5-6	0.16	77.36
Chitosan/Clay	13.92	11.56	3-4	3	3-4	3	3	3	3	3	3	3	6	0.14	83.05
PEI	14.24	12.95	4	4	3-4	3-4	3-4	3-4	3-4	4	4	4	6-7	0.14	90.94
PEI/Clay	15.18	13.84	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6-7	0.12	91.17

Treatment condition: Butantetracarboxylic acid (10 g/L); sodium hypophosphite (5 g/L); Polyamines (2 %); clay (0.5 %). Dyeing condition: dyeing time 120 min.; dyeing Temp. 70°C; L.R 1:50; pH 7

Table 8: CFU reduction (%) of bacterial and fungal strain cells for treated and dyed cotton fabrics using the shake flask method before and after washing

Treatment	Microbial Reduction					
	Escherichia coli		Staphylococcus aureus		Candida albicans	
	Before washing	After washing	Before washing	After washing	Before washing	After washing
Undyed						
Blank	Nil	Nil	Nil	Nil	Nil	Nil
Chitosan	88.59	79.64	96.68	91.00	43.08	38.97
Chitosan/Clay	64.13	57.65	72.05	67.82	38.37	34.71
PEI	95.10	85.49	76.10	71.63	73.55	66.54
PEI/Clay	88.19	79.28	71.02	66.85	57.71	52.21
Moringa						
Blank	59.43	55.21	48.79	45.32	38.39	36.11
Chitosan	86.28	80.15	98.76	91.74	45.03	42.35
Chitosan/Clay	63.64	59.12	55.02	51.11	51.33	48.28
PEI	94.53	87.81	86.42	80.28	98.20	92.36
PEI/Clay	83.73	77.78	84.55	78.54	99.05	93.16
Cochineal						
Blank	39.80	34.12	32.67	28.01	26.04	22.32
Chitosan	75.66	64.86	90.80	77.84	33.74	28.92
Chitosan/Clay	70.93	60.81	85.57	73.36	16.87	14.46
PEI	92.82	87.86	99.23	93.92	99.65	94.32
PEI/Clay	80.85	69.31	97.53	83.61	97.95	83.97

Table 7 showed the antibacterial activity of cotton-treated and dyed using two natural dyes. The results show that two types of bacteria and funguses that were tested on untreated cotton fabric had no inhibitory effects (blank). Dyeing untreated cotton fabric with both natural dyes reveals considerably enhanced antibacterial activity in comparison to the three types of microorganisms examined. This effective action is due to the presence of phenolic acids and flavonoids in extracts.

The treated fabrics are more efficient with gram-negative bacteria compared to gram-positive bacteria because both the investigated bacterial strain have different compositional differences in cell walls. These polyamines are also used to inhibit ergosterol which is known as a primary component of the fungal cell membrane. **[102-108]**

Treated fabric with PEI with/without clay has a stronger antibacterial effect than Treated fabric with chitosan with/without clay. This is because the presence of high amounts of amino groups plays a great role in attacking the microbial cell membrane and provides a strong antibacterial. **[47, 109]**

Metals in clay have interacted with the cells of the bacterium effectively through the coating process. Metals are well diffused and stabilized on the cotton surface by the polymers included in the cover, therefore limiting the ability to link bacterium cells to the cotton surface.**[59, 110-112]**

Moreover, treated and dyed cotton textiles are of superior antibacterial characteristics than untreated ones, before and after washing. In terms of polyamines with/without clay utilized for treatment, this drop in the percentage reduction is different. The durability of the textiles being processed offers an excellent antimicrobial property after washing against tested microorganisms.

4. Conclusion

Modification of cotton fabrics using polyamines in the presence and absence of clay was examined. Both treatments have led to a significant rise in cotton dyeing with cochineal and moringa as natural dyes. In addition, a reduction in temperature and dyeing time has been confirmed. Through the polyamine modification with and without clay, the color strength, fastness properties, dye leveling, and dye fixation of the cotton fabrics have been enhanced. The effective adhesion of polyamines to the surface of cotton fabrics was confirmed by the SEM pictures and the FTIR spectrum. This easy and ecologically safe approach might be an alternative to the standard cotton process of natural dyeing.

5. Conflict of interest

We confirm that there is no conflict of interest.

6. Acknowledgments

This research was supported financially by the National Research Centre, Egypt, through project No. 11090127. Furthermore, the authors are gratefully grateful to acknowledge the Central Labs Services (CLS) and Centre of Excellence for Innovative Textiles Technology (CEITT) in Textile Research and Technology Institute (TRTI), National Research Centre (NRC) for the facilities provided.

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