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STUDY ON PREPARATION OF ANTIBACTERIAL COTTON FABRICS USING *DIOSPYROL MOLLIS* FRUIT EXTRACT AND SOME OTHER ADDITIVES

SUMMARY OF DISSERTATION ON SCIENCES OF MATTER

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INTRODUCTION

1. The necessity of the thesis

In recent years, antibacterial textiles have been researched, developed, and industrially produced on a large scale to improve the quality of life and safety for humans. If the textiles have not the antibacterial ability are exposed to bacteria, for example, *E. coli* and *S. aureus*, they often have unpleasant odors, are prone to fading and damage, and can transmit diseases to users. These bacteria can cause health problems such as skin irritation upon contact, skin infections, sepsis, and other health problems. Amongst various fabrics, cotton is a commonly used material for producing clothing for adults, children, and especially infants due to its superior qualities such as high absorbance, softness, breathability, high durability, and skin-friendly nature. Antibacterial cotton fabric is utilized in the medical field for items like face masks, surgical clothing, cotton pads, wound dressings, etc. Antibacterial agents used for fabric can be organic or inorganic, with common organic sources being alkaloids, organic sulfur compounds, phenolic acids, flavonoids, carotenoids, coumarins, terpenes, tannins, as well as primary metabolites (amino acids, peptides, organic acids) from plants (leaves, bark, roots, fruits, and seeds) or chitosan from shrimp shells, crab shells, etc. Common inorganic antibacterial agents include metal nanoparticles, metal oxide nanoparticles, and their mixtures (Ag, Zn, Cu, Au, Ti, Pt, Fe, etc.), as well as zeolite/Ag, zeolite/Zn, Ag-Zn/zeolite complexes, etc. These antibacterial agents have been studied independently and combining inorganic and organic antibacterial agents extracted from plant extracts used in cotton fabric has not been considered. In Vietnam, the source of plant-derived antibacterial agents is rich and diverse, with the *Diospyrol mollis* fruits traditionally used by locals to treat fabric dyes. After treatment, the treated fabric gains valuable properties, especially antibacterial activity and UV-resistant ability. Using *Diospyrol mollis* fruit extract for the treatment of cotton fabric contributes has advantage of available raw materials, partially replacing synthetic dyes, reducing environmental pollution, creating friendly, safe products, and developing traditional craft villages in Vietnam. Therefore, PhD candidate has chosen the project *"Study on preparation of antibacterial cotton fabric using Diospyrol mollis fruit extract and some other additives"* to exploit the antibacterial properties of natural ingredients combined with commercial inorganic antibacterial substances to enhance the quality of antibacterial cotton fabric, including durability and other ecological properties.

2. Objective of the thesis

- Having data of content of tannins, diospyrol, and saponins in *Diospyrol mollis* (DM) fruit extracts and antibacterial activity of these compounds.

- The optimal conditions for the cotton fabric treatment process using the DM fruit extract will be found to improve the antibacterial ability against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli (E. coli)*.
- The appropriate component ratio of the antibacterial mixture (DM fruit extract/water, Ag-Zn/zeolite content, tannin content) will be determined for the treatment of cotton fabric as well as optimal technological factors to process cotton fabric to reach antibacterial efficiency against *E. coli* and *S. aureus* bacteria by over 98 %.
- The treated cotton fabric will be produced with good mechanical properties, high UV resistance, and color fastness, meeting safety requirements for users and environmentally friendly through processing with the DM fruit extract combined with tannin and Ag-Zn/zeolite.

3. The main research contents of the thesis

- Extracting and determining the content of tannins, diospyrol, and saponins in DM fruits.
- Study on the antibacterial ability of the DM fruit extract against two bacterial strains of *E. coli* and *S. aureus*.
- Optimize the cotton fabric treatment process with the DM fruit extract to achieve the cotton fabric having a high antibacterial ability.
- Optimize the composition ratio of the mixture (DM fruit extract, Ag-Zn/zeolite, and tannin) to treat the cotton fabric having an effective antibacterial ability.
- Study on the synergistic effectiveness achieved for antibacterial cotton fabric when combining the DM fruit extract with Ag-Zn/zeolite and tannin.

4. Layout of the thesis

The thesis comprises 106 pages, 71 figures, 41 tables, 140 references, and 21 appendices. The thesis structure includes the following parts: Introduction, 3 chapters of content, and conclusion. The results of the thesis have been published in 2 articles (in SCIE international journals Q1 and Q2), 01 article has been accepted for publication on August 23, 2024 (in Vietnam Journal of Science and Technology).

CHAPTER 1. OVERVIEW

Chapter 1 is presented in 31 pages with 25 figures and 08 tables. From the overview of the international and national research, it can be seen that cotton fabric production using extract compounds from DM fruits combined with environmentally friendly organic and inorganic antibacterial agents has contributed to enhancing antibacterial durability, improving mechanical properties, UV resistance, etc., for cotton fabrics. Research on antibacterial cotton fabrics involves a main, effective solution such as using single agents such as inorganic antibacterial agents (Au, Ag, Ti, Zn, Cu, etc.) in the form of metal nanoparticles, oxide or mixture nanoparticles; betel leaf extracts, green tea extracts, etc.; polymers like chitosan, N-halamine-based polymers, etc. However, the combination of the DM fruit extract with Ag-Zn/zeolite and tannin for cotton fabric treatment has not been reported. Antibacterial treatment using the DM fruit extract and a mixture including DM fruit extract/water, Ag-Zn/zeolite, tannin, and improving durability and other ecological properties of cotton fabric are the objectives of this thesis.

CHAPTER 2. EXPERIMENTAL

Chapter 2 is presented in 28 pages, 22 figures, and 05 tables including sections:

2.1. Research subject

2.1.1. Materials and chemicals

2.1.2. Main equipment and devices

2.2. Research methods

2.2.1. Extraction and preparation of extract from fresh DM fruit with ultrasonic vibration assistant

2.2.2. Extraction and preparation of extract from dried DM fruit with ultrasonic vibration assistant

2.2.3. Determination of tannin, diospyrol, and saponin content in the extract from dried DM fruits

2.2.4. Cotton fabric processing and technological process optimization

2.2.4.1. Optimization of the cotton fabric treatment process with DM fruit extracts

2.2.4.2. Optimization of mixture component ratios for processing cotton fabrics

2.2.4.3. Processing cotton fabric with the mixture

2.2.5. Dyeing cotton fabric with reactive dyes

2.2.6. Setting up the procedure for production of anti-bacterial cotton fabric

2.2.7. Determination of the antibacterial activity of cotton fabric

2.2.8. Determination of the antibacterial activity of the extract from the fruit

2.2.9. Determination of other properties of cotton fabric after treatment

CHAPTER 3. RESULTS AND DISCUSSION

Chapter 3 is presented in 47 pages, 23 figures, and 28 tables including sections:

3.1. Contents of some compounds in DM fruits and the antibacterial ability of the DM extracts

In this study, the main organic compounds in the DM fruit extract including saponins, tannins, and diospyrol were determined and presented in Table 3.1. The tannin content is the highest (9.98 %), followed by saponin (16.3 %) and diospyrol (0.12 %).

Table 3.1. Composition of some compounds in DM dried fruit extract

No.	Compound	Unit	Content
1	Tannin	%	9.98
2	Diospyrol	%	0.12
3	Saponin	%	16.3

The DM fruits have the moisture content of 68.89%, thus, from the data in Table 3.1, it is possible to extrapolate the tannin content in the fresh DM fruit extract to be about 9.98%. The tannin content in the extract in this study is equivalent to previously published results such as the report of Do Tat Loi (the average tannin content in DM fruits in Vietnam is about 10%) [6]. Meanwhile, the tannin content in Thailand DM fruit is about 12 - 15% [97]. Some fruits related to the genus Diospyros have a relatively high tannin content, for example, the *Diospyros Mespiliformis* fruit extract in acetone from 100 g of dried *Diospyros Mespiliformis* fruits contains 13.52g of tannin [98], or the tannin content in the fruits of *Diospyros decandra*, *Diospyros rhodocalyx*, *Diospyros gracilis* were 27.6%, 21.8%, 21.1%, respectively [99]. The aponin has the common characteristic that when dissolved in water, it will reduce the surface tension of the solution and create a lot of foam [100]. Therefore, saponin as a biosurfactant is used in the cotton fabric treatment process without the need to add surfactants like the cotton fabric dyeing process with reactive dyes. Because it is available in the DM fruit, saponin contributes to reducing environmental pollution. According to Mongkolsuk et al., diospyrol is a polyhydroxybinaphthyl compound in the DM fruit, it is highly oxidized in the air, so it will turn black when exposed to air and light, the oxidation process of diospyrol occurs continuously [101]. Tannin extracted from the fruit of the plant was evaluated for its antibacterial ability against two strains of bacteria, *E. coli* and *S. aureus* (Table 3.2, Figures 3.1, 3.2).

From the data in Table 3.2, it can be seen that the tannin extract from the DM fruit has reduction rate for *E. coli* and *S. aureus* bacteria strains reaching 88.90 % and 90.05 %, respectively. The total extract of DM fruits has reduction rate for *E. coli* and *S. aureus* reaching 99.90 %. The reduction rates for *E. coli* and *S. aureus* bacteria of the solution extract from dried DM fruits are 81.62 % and 82.36 %, respectively. The reduction rates for *E. coli* and *S. aureus* bacteria of the solution extract from fresh DM fruits are 96.65 % and 92.29 %, respectively. It can be seen that in the DM fruit, tannins, diospyrol and some other organic compounds also have antibacterial properties against *E. coli* and *S. aureus*. The total extract from the DM fruit has the best antibacterial properties. This may be due to the combined antibacterial properties of many organic compounds such as tannins, diospyrol, polyphenols, alkaloids, sterols, etc. [102, 103]. With the same ratio of input materials, the extract from dried

DM fruit has a lower antibacterial property than the extract from fresh DM fruit because during the drying process, under the influence of temperature and evaporation of water, a number of heat-sensitive organic compounds can be decomposed and lost, and organic compounds can also be transformed during long-term exposure to heat. Diospyrol in the DM fruit can be oxidized, contributing to the reduction of the antibacterial activity of the solution extract from dried DM fruit.

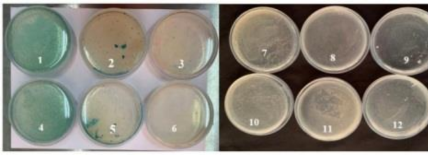


Figure 3.1. Images of agar dishes containing the fresh DM extract in the antibacterial test

Figure 3.2. Images of agar dishes containing the dried DM extract in the antibacterial test

Table 3.2. Antibacterial activity of tannin and the extracts from DM fruits

Parameters			**Result**
Tannin extract (a concentration of 2 % by weight)	*E. coli*	0 hour, CFU/sample	$1.8x\ 10^5$
		24 hours, CFU/sample	2.0×10^4
		% reduction rate	**88.90**
	S. aureus	0 hour, CFU/sample	1.8×10^5
		24 hours, CFU/sample	1.8×10^4
		% reduction rate	**90.50**
Total extract from dried DM fruits (a concentration of 2 % by weight)	*E. coli*	0 hour, CFU/sample	1.9×10^5
		24 hours, CFU/sample	1.4×10^3
		% reduction rate	**99.99**
	S. aureus	0 hour, CFU/sample	1.8×10^5
		24 hours, CFU/sample	1.4×10^3
		% reduction rate	**99.99**
The extract from dried DM fruits (a concentration of 2 % by volume)	*E. coli*	0 hour, CFU/sample	1.5×10^5
		24 hours, CFU/sample	1.3×10^3
		% reduction rate	**81.62**
	S. aureus	0 hour, CFU/sample	1.4×10^5
		24 hours, CFU/sample	1.2×10^3
		% reduction rate	**82.36**
The extract from fresh DM fruits (a concentration of 2 % by volume)	*E. coli*	0 hour, CFU/sample	1.9×10^5
		24 hours, CFU/sample	1.6×10^3
		% reduction rate	**96.65**
	S. aureus	0 hour, CFU/sample	1.9×10^5
		24 hours, CFU/sample	1.2×10^3
		% reduction rate	**92.29**

3.2. Selecting the extract from DM fruits for treatment of cotton fabric to meet antibacterial requirements

From the results in Table 3.3, it can be seen the L* value of the cotton fabric treated with the extract from dried DM fruits reaches 74.36 while that of the cotton fabric treated with the extract from fresh DM fruits reached 73.08. This suggests that the color of the cotton fabric treated with the dried DM fruit extract is lighter than that of the cotton fabric treated with the fresh DM fruit extract. The color change (ΔE*) of the cotton fabric treated with the dried DM fruit extract is 6.23, a difference from that of the cotton fabric treated with the fresh DM fruit extract by 75.17 %. The K/S value of the cotton fabric treated with the fresh DM fruit extract is 0.45, a difference from that of the cotton fabric treated with the dried DM fruit extract by 97.57 %.

Table 3.3. Color change of cotton fabric treated with extracts from dried and fresh DM fruits

Cotton fabric	**L***	**a***	**b***	**C***	**H***	**ΔE***	**K/S**	**Photo of samples**
Untreated	90.00 ± 0.02	1.11 ± 0.01	7.60 ± 0.01	7.69 ± 0.01	81.70 ± 0.02		0.07	
Treated with dried DM fruit extract	74.36 ± 0.02	2.41 ± 0.01	9.90 ± 0.01	10.19 ± 0.01	76.92 ± 0.02	6.23 ± 0.01	0.45	
Treated with fresh DM fruit extract	20.02 ± 0.02	3.36 ± 0.01	4.46 ± 0.01	5.58 ± 0.01	52.96 ± 0.02	25.09 ± 0.01	18.52	

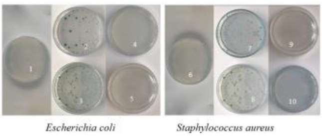


Figure 3.3. Images of agar dishes containing the suspension of cotton fabric treated with fresh DM fruit extract

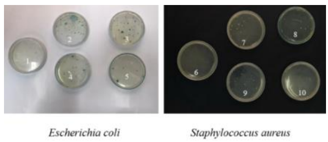


Figure 3.4. Images of agar dishes containing the suspension of cotton fabric treated with dried DM fruit extract

Table 3.4. Antibacterial activity of the dried DM fruit extract and cotton fabric treated with the dried DM fruit extract

Parameters			**Result**
The bacterial reduction rate of the dried DM fruit extract	*E. coli*	0 hour, CFU/sample	1.5 x 10^5
		24 hours, CFU/sample	1.3 x 10^3
		% reduction rate	**81.62**
	S. aureus	0 hour, CFU/sample	1.4 x 10^5
		24 hours, CFU/sample	1.2 x 10^3
		% reduction rate	**82.36**
The bacterial reduction rate of the cotton fabric treated with the dried DM fruit extract	*E. coli*	0 hour, CFU/sample	1.6 x 10^5
		24 hours, CFU/sample	1.3 x 10^3
		% reduction rate	**18.60**
	S. aureus	0 hour, CFU/sample	1.3 x 10^5
		24 hours, CFU/sample	1.1 x 10^3
		% reduction rate	**22.30**

Figures 3.3 and 3.4, Tables 3.4 show that the activity to kill *E. coli* and *S. aureus* bacteria of the cotton fabric treated with the extract from fresh DM fruits is better than that of the cotton fabric treated with the extract from dried DM fruits, with a difference in reduction rates for *E. coli* and *S. aureus* by

81.40 % and 77.70 %, respectively. This may be due to the dried DM fruit is harder than the fresh DM fruit, making it more difficult to separate antibacterial compounds such as tannin, diospyrol, diospyrol and some other antibacterial organic compounds, so they are little or not adsorbed onto the cotton fabric during the treatment process, causing the antibacterial ability of the cotton fabric after treatment with the extract from the dried fruit of the plant to decrease sharply. Therefore, with its good color and antibacterial ability, the extract from the fresh DM fruit is chosen for antibacterial treatment of cotton fabric.

3.3. Optimize the cotton fabric treatment process and optimize the mixed composition ratio for the cotton fabric treatment

3.3.1. Optimize the cotton fabric treatment process using the DM fruit extract

Analysis of variance (ANOVA) results in Table 3.5 indicate that the high regression coefficient (R^2) (96.94 - 97.88 %) confirms suitability between two objective functions, Y1 (killed *S. aureus* percentage), and Y2 (killed *E. coli* percentage) according to technological variables/factors such as X1 (treatment temperature), X2 (treatment time), X3 (the ratio of DM fruit extract with water), and the quadratic equation. The adjusted R^2 coefficients for Y1 and Y2 are 95.63 % and 96.69 %, respectively. These values are close to 100 % showing that the selected model is highly compatible with the experimental data. Additionally, the high Fisher standard values (F = 107.49 for Y1 and F = 73.94 for Y2) also confirm a high compatibility between this model with the experiment. The quadratic model has high statistical significance with a p-value of <0.05.

Table 3.5. ANOVA results for objective functions

Source	Killed *S. aureus* percentage		Killed *E. coli* percentage	
	F-value	p-value	F-value	p-value
Model	73.94	0.000	107.49	0.000
Linear	85.70	0.000	127.11	0.000
X1 (ºC)	150.20	0.000	229.75	0.000
X2 (minutes)	0.87	0.367	1.39	0.259
X3 (v/v)	120.22	0.000	171.12	0.000
Square	28.94	0.000	41.99	0.000
$(X1)^2$ $(^oC)^2$	71.21	0.000	107.10	0.000
$(X2)^2$ $(minutes)^2$	0.04	0.835	0.02	0.895
$(X3)^2$ $(v/v)^2$	19.26	0.001	22.20	0.000

The quadratic equations corresponding to Y1 and Y2 objective functions that are according to the technological variables/factors X1, X2, X3 (Table 3.6, Figure 3.5) are:

$$Y1 (\%) = -144.3 + 5.551X1 + 0.241X2 + 160.9X3 - 0.04936(X1)^2 - 0.00111(X2)^2 - 90.3(X3)^2 \quad (3.1)$$

$$Y2 (\%) = -136.3 + 5.482X1 + 0.178X2 + 146.2X3 - 0.04884(X1)^2 - 0.00057(X2)^2 - 78.2(X3)^2 \quad (3.2)$$

Table 3.6. Coefficients of the quadratic equation corresponding to the objective functions and the corresponding ANOVA

Term	**Killed *S. aureus* percentage**					**Killed *E. coli* percentage**				
	Coef	SE Coef	T-Value	P-Value	VIF	Coef	SE Coef	T-Value	P-Value	VIF
Constant	71.17	2.77	25.2	0.000		70.62	2.23	31.62	0.000	
X1 (°C)	-40.76	3.33	-12.26	0.000	1.08	-40.68	2.68	-15.16	0.000	1.08
X2 (minutes)	3.22	3.46	0.93	0.367	1.00	3.29	2.79	1.18	0.259	1.00
X3 (v/v)	34.53	3.15	10.96	0.000	1.40	33.24	2.54	13.08	0.000	1.40
$(X1)^2$ $(°C)^2$	-44.42	5.26	-8.44	0.000	1.16	-43.96	4.25	-10.35	0.000	1.16
$(X2)^2$ $(minutes)^2$	-1.00	4.72	-0.21	0.835	1.17	-0.51	3.81	-0.14	0.895	1.17
$(X3)^2$ $(v/v)^2$	-22.12	5.04	-4.39	0.001	1.44	-19.16	4.07	-4.71	0.000	1.44

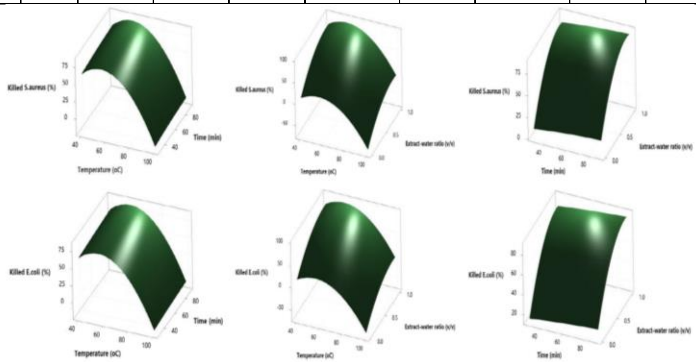


Figure 3.5. Graphs of response surface reflecting the dependence of objective functions on technological variables

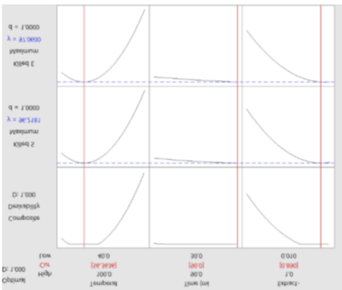


Figure 3.6. Desirability level of objective functions under optimal condition

Thus, the optimal condition for the process of treating the cotton fabric with DM fruit extract to achieve the highest antibacterial ability of the treated cotton fabric include a temperature of 56.5 °C, a time of 90 minutes, and a DM fruit extract/water ratio of 89/100 (v/v) (Figure 3.6).

The results of checking the suitability between the prediction, and actual experiments under optimal conditions for 2 objective functions (killed *E. coli* percentage and killed *S. aureus* percentage) in Table 3.7 show a good agreement. For instance, the killed *E. coli* percentage and killed *S. aureus* percentage of cotton fabric treated with DM fruit extract under optimal conditions reached 99.9 % and 99.9 %, respectively, close to the corresponding predicted values, 96.22 % and 97.06 %. Therefore, the optimal model is consistent with the experiment.

From the optimal solution, the procedure for the production of antibacterial cotton fabric is presented in Figure 3.7.

Table 3.7. Optimal technological condition and theoretical and experimental values of objective function at optimal condition

Optimal condition			Objective functions	Results	
Temperature (^{0}C)	Time (minutes)	DM fruit extract/water ratio (v/v)		Prediction	Actual
56.5	90	0.89	Killed S. aureus (%)	96.22	99.9
			Killed E. coli (%)	97.06	99.9

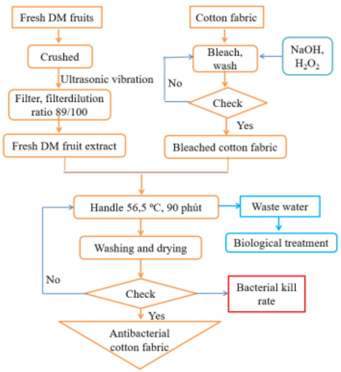


Figure 3.7. Procedure for treatment of the antibacterial cotton fabric

- Technology application:
+ Cotton fabric: M (kg)
+ NaOH: a (gam)
+ H_2O_2: b (ml)
+ Fresh DM fruits: M (kg)
+ The ratio of DM fruit weight/water (w/v): 1/2
+ The ratio of DM fruit extract/water (v/v): 89/100
+ Treatment temperature: 56.5 (ºC)
+ Treatment time: 90 (minutes)
+ pH: 4.5
+ The ratio of fabric cotton/solution: 1/20 (w/v)

3.3.2. Optimize the composition ratio of the mixture for the treatment of the cotton fabric

Values of Zeta potentials of 15 samples that were treated according to the change in the ratio of DM fruit extract to water (A), Ag-Zn/zeolite content (B), tannin content (C) according to Box-Benhken design (BBD) are presented in Tables 3.8 - 3.9. It can be seen that these samples are highly stable with Zeta potential values less than - 40 mV. ANOVA indicates an F-value of 9.56 with a p-value < 0.05. In addition, the regression value (R^2) of this model is 0.945 and the adjusted R^2 value is 0.846 while the p-value of "Lack of fit" is 0.217, much higher than 0.05. The obtained results show that the Zeta potential values of the 15 mixtures have complied with the quadratic model. After removing the insignificant factors, the quadratic equation for the Zeta potential of the mixture was presented as Eq. (3.3).

$$\text{Zeta potential (mV)} = -43.4333 + 0.6875B + 0.729167 A^2 + 0.929167 B^2 \quad (3.3)$$

Table 3.8. Zeta potential of 15 experiments designed by BBD

No.	The ratio of DM fruit extract/water (v/v), A	Ag-Zn/zeolite content (%), B	Tannin content (%), C	Zeta potential (mV) ± 0.2; Y
1	0.87	0.05	0.1	-42.7
2	0.91	0.05	0.1	-42.7
3	0.87	0.15	0.1	-40.7
4	0.91	0.15	0.1	-41.0
5	0.87	0.1	0.05	-42.7
6	0.91	0.1	0.05	-42.3
7	0.87	0.1	0.15	-41.6
8	0.91	0.1	0.15	-42.8
9	0.89	0.05	0.05	-42.9
10	0.89	0.15	0.05	-41.8
11	0.89	0.05	0.15	-42.3
12	0.89	0.15	0.15	-42.7
13	0.89	0.1	0.1	-43.5
14	0.89	0.1	0.1	-43.0
15	0.89	0.1	0.1	-42.8

Table 3.9. ANOVA results for Zeta potential

Source	Sum of Squares	Df	Mean Square	F-value	P-value
Model	9.88	9	1.1	9.56	0.0114
A-A	0.1512	1	0.1512	1.32	0.3030
B-B	3.78	1	3.78	32.93	0.0023
C-C	0.245	1	0.245	2.13	0.2039
AB	0.0225	1	0.0225	0.1959	0.6765
AC	0.640	1	0.640	5.57	0.0647
BC	0.040	1	0.040	0.3483	0.5807
A^2	1.96	1	1.96	17.10	0.009
B^2	3.19	1	3.19	27.76	0.0033
C^2	0.4631	1	0.4631	4.03	0.1009
Residual	0.5742	5	0.114		
Lack of Fit	0.4875	3	0.162	3.75	0.2176
Pure Error	0.0867	2	0.043		
Cor Total	10.46	14			
R^2	0.9451				
Adjusted R^2	0.8462				
Adeq Precision	9.2463				

The graphs of the Zeta potential distribution according to prediction and experiment as well as the response surface of double interaction effects of technology variables on the Zeta potential of mixture and desirability of Zeta potential are presented in Figures 3.8 and 3.9. As obtained from the optimization process, one set of optimal conditions was found with a predicted value of the Zeta potential of the mixture was -43.59 mV (Figure 3.10). The optimal conditions include the ratio of DM fruit extract to water of 89/100, Ag-Zn/zeolite content of 0.083 %, and tannin content of 0.085 %, respectively.

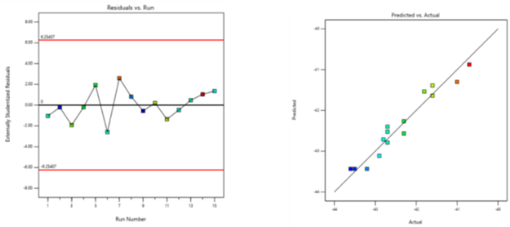


Figure 3.8. Graphs of Zeta potential distribution of prediction and experiment

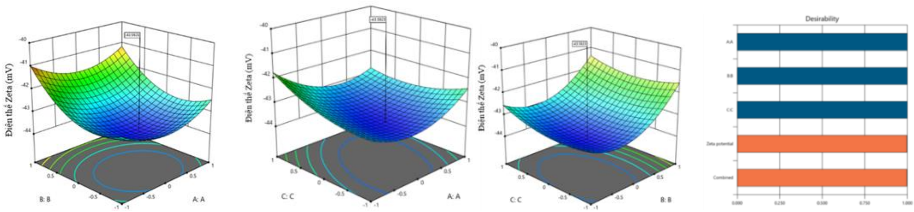


Figure 3.9. Response surface of double interaction effects of technology variables on Zeta potential of mixture and desirability of Zeta potential

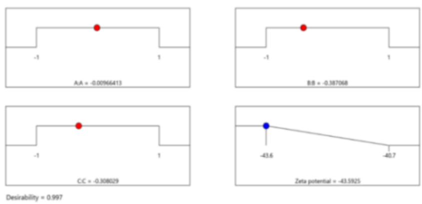


Figure 3.10. Slope plot of optimal objective function

In order to check the suitability of the prediction and actual, three experiments were carried out under optimal conditions. The obtained results in Table 3.10 indicate that the actual Zeta potential of the mixture for the treatment of the cotton fabric under optimal conditions ranged from -42.8 mV to -43.5 mV (RSD < 2 %). So, there is a good suitability between prediction and actual Zeta potential. The mixture of DM fruit extract/water (89/100 v/v), Ag-Zn/zeolite (0.083 %), and tannin (0.085 %) with the optimal composition (abbreviated as the optimal mixture) has been used for treating the antibacterial cotton fabric.

Table 3.10. Zeta potential of the mixture under optimal conditions

No.	Optimal conditions			Actual	Prediction	RSD (%)
	Ratio of DM fruit extract/water (v/v)	Ag-Zn/zeolite content (%)	Tannin content (%)	Zeta potential (mV)	Zeta potential (mV)	
1	89/100	0.083	0.085	-43.0	-43.59	1.35
2	89/100	0.083	0.085	-43.5	-43.59	0.23
3	89/100	0.083	0.085	-42.8	-43.59	1.81

With the optimal composition, the following procedure for the treatment of antibacterial cotton fabric has been applied.

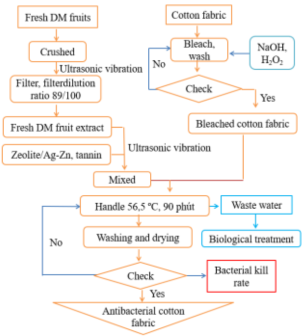


Figure 3.11. Procedure for treatment of cotton fabric with the optimal mixture

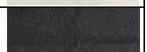
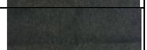
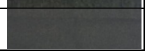
- Technology application:
+ Cotton fabric: M (kg)
+ NaOH: a (gam), H_2O_2: b (ml)
+ Fresh DM fruits: M (kg)
+ The ratio of DM fruit weight/water (w/v): 1/2
+ The ratio of DM fruit extract/water (v/v): 89/100
+ Zeolite Ag/Zn: 0.083 %, tannin: 0.085 % (comparison with the cotton fabric weight)
+ Treatment temperature: 56.5 (ºC)
+ Treatment time: 90 (minutes)
+ pH: 4.5
+ The ratio of fabric cotton/solution: 1/20 (w/v)

3.4. Characteristics and properties of antibacterial cotton fabrics

3.4.1. Dyeing capacity

The color change of treated cotton fabric samples can be distinguished through color parameters as displayed in Table 3.11. The DM fruit extract, reactive dye and optimal mixture exhibit a great dyeing capacity with L* values reaching 20.02, 20.68, and 26.78, respectively while the ΔE* values of the cotton fabric treated with DM fruit extract, reactive dye and optimal mixture are 25.09, 21.52, and 22.51, respectively. Thus, the above agents are all capable of treating color for the cotton fabric.

Table 3.11. Color change of cotton fabrics treated with the DM fruit extract, reactive dye, and optimal mixture

Cotton fabric	L*	a*	b*	C*	H*	ΔE*	K/S	Photo of samples
Untreated	90.00 ± 0.02	1.11 ± 0.01	7.60 ± 0.01	7.69 ± 0.01	81.70 ± 0.02	0	0.07	
Treated with the DM fruit extract	20.02 ± 0.02	3.36 ± 0.01	4.46 ± 0.01	5.58 ± 0.01	52.96 ± 0.02	25.09 ± 0.01	18.52	
Treated with reactive dye	20.68 ± 0.02	3.56 ± 0.01	7.78 ± 0.01	5.96 ± 0.01	53.32 ± 0.02	21.52 ± 0.01	19.36	
Treated with the optimal mixture	26.78 ± 0.02	2.56 ± 0.01	4.85 ± 0.01	5.49 ± 0.01	62.21 ± 0.02	22.51 ± 0.01	16.09	

3.4.2. Morphology of treated cotton fabrics

Scanning electron microscopy (SEM) images of the cross-sectional surface of cotton fabrics before and after being treated with DM fruit extract and the optimal mixture are presented in Figure 3.12.

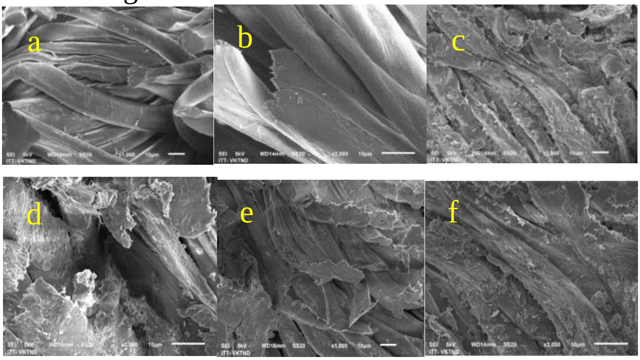


Figure 3.12. SEM images of cotton fabric before treatment (a, b), after treatment with the fresh DM fruit extract (c, d) and after treatment with the optimal mixture (e, f), magnification of 1000 and 2000 times

It can be seen an obvious difference in the morphology of these samples. For instance, the untreated cotton fabric exhibits a smooth surface while the treated cotton fabric has a rough surface. The variation in the surface of treated cotton fabric samples is caused by the presence of organic substances such as color-carrying compounds such as diospyrol, antibacterial agents such as tannins, saponins, diospyrol, and other compounds in the DM fruit extract as well as the presence of Ag-Zn/zeolite and tannins that have been absorbed deep into the structure and adhered to the surface of cotton fibers. They can interact and link with cellulose macromolecules, penetrating deeply into the capillary structure of cotton fibers, leading to changes in the morphology and structure of the cotton fabric.

3.4.3. Infrared spectra of treated cotton fabrics

Figure 3.13 reveals IR spectra of DM fruit extract, untreated cotton fabric, and cotton fabric treated with the DM fruit extract. The bands characterized for vibrations of functional organic groups in the IR spectrum of the DM fruit extract include O-H linkage in tannins, diospyrol, and saponins at a wavenumber of 3316 cm^{-1}, C=O linkage in COOH in tannins and C=C linkage in the aromatic ring at wavenumbers of 1641 cm^{-1} and 1609 cm^{-1}. Besides, vibrations of C-H, C-O, and C-C linkages are found at 2924 cm^{-1}, 1379 cm^{-1}, and 1046 cm^{-1}, respectively.

The IR spectrum of the untreated cotton fabric exhibits the vibrations of O-H, C-H, and C-C linkages in cellulose. After being treated with the DM fruit extract, the intensity and position of O-H and C=O bands were changed slightly. For example, as compared to the IR spectrum of the untreated cotton fabric, the bending vibration of the O-H linkage in the IR spectrum of the treated cotton fabric shifted from 1641 cm^{-1} to 1631 cm^{-1}. This may be due to the overlap of the bending vibration of the O-H linkage in cellulose with the stretching vibration of the C=O linkage in the DM fruit extract. This is evidence for the treatment of the cotton fabric with the DM fruit extract.

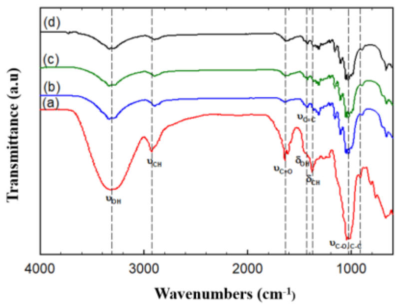


Figure 3.13. IR spectra of the fresh DM fruit extract (a), cotton fabric before treatment (b), after treatment with the fresh DM fruit extract (c) and after treatment with the optimal mixture (d)

Figure 3.13 also presents the IR spectrum of the cotton fabric treated with the optimal mixture. It can be seen the appearance of vibrations characterized for O-H, C-O, C=O, C-H, and C-C linkages in the optimal mixture and cellulose in the wavenumbers ranging from 4000 cm^{-1} to 400 cm^{-1}. Importantly, the dyeing process did not lead to changes in the functional groups of the cotton fabrics.

The vibration of organic molecules in the optimal mixture is not separated due to the overlap of the vibration of functional groups of cellulose. Thus, the optimal mixture and the cotton fabric interacted with each other.

3.4.4. UV resistance ability of treated cotton fabrics

As observed in Table 3.12, the transmittance percentage values of UV-A (315 nm - 400 nm) and UV-B (290 nm - 315 nm) rays of the cotton fabric treated with the DM fruit extract reach 0.08 %, and 0.05 %, respectively. Those values of the cotton fabric treated with the optimal mixture are 1.98 %, and 1.28 % while those of the untreated cotton fabric are 12.46 %, and 8.54 %, respectively. Thus, the UV resistance ability of the treated cotton fabric samples is much higher than that of the untreated cotton fabric. This can be explained by the organic compounds in the DM fruit extract can cover the surface of cotton fibrils, helping to limit UV ray transmittance. Moreover, the UV absorbance ability of polyphenolic compounds and diospyrol that remain on the cotton fiber after treatment contributes to enhancing the UV resistance ability of the treated cotton fabric samples. Furthermore, tannin – the main component in the DM fruit extract can act as a UV shield when adhesion on the surface of cotton fibrils. Additionally, the porous structure of Ag-Zn/zeolite combined with organic compounds in the DM fruit extract can absorb UV rays and act as a stabilizer for cellulose macromolecules in the cotton fabric. The illustration of UV protection of antibacterial treated cotton fabric is presented in Figure 3.14.

Table 3.12. UV resistance ability of untreated and treated cotton fabric samples

Cotton fabric sample	UPF	Transmittance UV-A (%)	Transmittance UV-B (%)
Untreated	10.25	12.46	8.54
Treated with DM fruit extract	54.08	0.08	0.05
Treated with optimal mixture	52.20	1.98	1.28

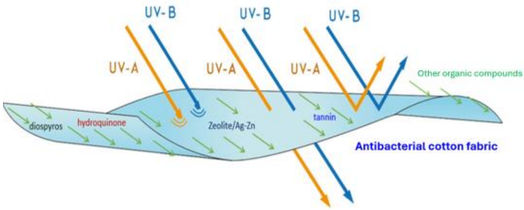


Figure 3.14. Illustration of UV protection of antibacterial-treated cotton fabric

3.4.5. Air permeability of treated cotton fabric

The data in Figure 3.15 indicate the air permeability of the cotton fabric treated with the DM fruit extract and the optimal mixture reduced by 42.19 % and 36.55 %, respectively.

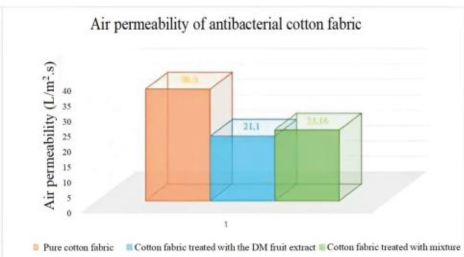


Figure 3.15. Air permeability of the antibacterial-treated cotton fabric

This is due to small molecules in the DM fruit extract, tannin, and Ag-Zn/zeolite going deep into the capillaries of cotton fibers, into the interlayer area between the cotton fibers, and filling the gaps of the textile fibers in the fabric. However, the treated cotton fabric samples still meet the requirement of the standard about air permeability.

3.4.6. Water vapor absorption of treated cotton fabric

Figure 3.16 performs the water vapor absorption of the untreated and treated cotton fabric samples. The water vapor absorption of the treated cotton fabric samples increased slightly (5.17 %-5.27 %) as compared to that of the untreated cotton fabric. This can be explained by organic molecules such as saponins, tannins, and diospyrol on the surface of cotton fibrils can interact with water molecules thanks to their polarity and hydrophilic properties. On the other hand, the microstructure of the cotton fabrics dyed with the DM fruit extract is tighter than that of the untreated cotton fabric as shown in SEM images.

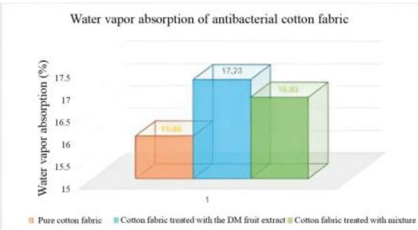


Figure 3.16. Water vapor absorption of the antibacterial-treated cotton fabric

When adding Ag-Zn/zeolite into the optimal mixture for the treatment of the cotton fabric, the water vapor absorption of the treated samples was reduced slightly.

3.4.7. Weight of treated cotton fabric

The results in Figure 3.17 demonstrate that the weight per unit area of treated cotton fabric samples increased strongly, from 12.04 % -14.42 % as compared to that of the untreated cotton fabric. This can be explained by the small molecules of saponin, tannin, diospyrol, and Ag-Zn/zeolite penetrating deeply into the cotton capillaries, into the interstitial area between the cotton structures, and filling the gaps of the cotton fabric. At the same time, they also interact or bind with cellulose macromolecules in cotton fibers.

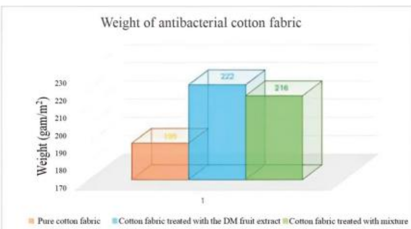


Figure 3.17. The weight per unit area of the antibacterial-treated cotton fabric

The ability to form films on cotton fibers treated with the optimal mixture decreased, leading to a decrease in the weight per unit of the treated cotton fabric.

3.4.8. Tensile strength and elongation at break of treated cotton fabric

From the data in Tables 3.13 and 3.14, it can be seen that, in the warp direction, the tensile strength and elongation at break of the cotton fabric treated with the DM fruit extract increased by 22.3 % and 19.5 %, respectively, while the cotton fabric treated with the optimal mixture increased by 16.8 % and 17.2 %, respectively, as compared to the untreated cotton fabric. In the weft direction, the tensile strength and elongation at break of the cotton fabric treated with the DM fruit extract increased by 29.1 % and 25.8 %, respectively, and that of the cotton fabric treated with the optimal mixture increased by 17.6 % and 18 %, respectively, as compared to the untreated cotton fabric.

The increase in the tensile strength and elongation at break of the treated cotton fabric samples may be attributed to tannins in the DM fruit extract binding and interacting with the OH groups of cotton fabric through hydrogen and Van der Waals bonds, leading to an enhancement in the mechanical properties of the treated cotton fabric samples. Additionally, organic compounds in the DM fruit extract and Ag-Zn/zeolite penetrating and locating within the cotton fibers make the fabric structure tighter, contributing to improved mechanical properties of the cotton fabric post-treatment with the DM fruit extract and the mixture in both warp and weft directions of the cotton fabric.

Table 3.13. Tensile strength and elongation at break of cotton fabrics treated and untreated in warp direction

Cotton fabric	Tensile strength (Nm)					Elongation at break (mm)				
	Warp direction					Warp direction				
	L1	L2	L3	TB	Increase (%)	L1	L2	L3	TB	Increase (%)
Untreated	519	519	518	519	0	56.16	56.16	56.38	56.23	0
Treated with DM fruit extract	668	667	668	668	22.3	69.89	69.88	67.90	69.89	19.5
Treated with optimal mixture	625	624	624	624	16.8	67.91	67.92	67.90	67.91	17.2

Table 3.14. Tensile strength and elongation at break of cotton fabrics treated and untreated in the weft direction

Cotton fabric	Tensile strength (Nm)					Elongation at break (mm)				
	Weft direction					Weft direction				
	L1	L2	L3	TB	Increase (%)	L1	L2	L3	TB	Increase (%)
Untreated	309	308	309	309	0	33.50	33.39	33.50	33.45	0
Treated with DM fruit extract	436	435	436	436	29.1	45.09	45.18	45.12	45.23	25.8
Treated with optimal mixture	365	374	375	375	17.6	40.80	40.78	40.79	40.79	18

3.4.9. Color fastness to washing, rubbing, and light of treated cotton fabric

The data in Tables 3.15 and 3.16 indicate that the treated cotton fabric samples exhibit a great color fastness to washing, rubbing, and light. After 30 washing cycles, the color fastness of both treated cotton fabric samples was reduced to two levels (Table 3.15). It can be explained by the soap solution partially removing diospyrol and tannins on the cotton fabric, washing away the organic compounds that adhered to the cotton surface during the washing process.

However, the soap does not strongly influence on the organic compounds, Ag-Zn/zeolite deep inside the cotton fibers, thus, the treated cotton fabric samples still reach level 3 color fastness after 30 washing cycles.

Table 3.15. Color fastness to washing treated cotton fabric

Cotton fabric	**Unit**	**Washing cycles/Color fastness to washing**			
		1	**10**	**20**	**30**
Treated with DM fruit extract	Level	5	4	3-4	3
Treated with optimal mixture	Level	5	4	3-4	3

Table 3.16. Color fastness to rubbing and light of treated cotton fabric

Cotton fabric	**Unit**	**Color fastness to rubbing**	**Color fastness to light**
Treated with DM fruit extract	Level	4/5	7/7
Treated with optimal mixture	Level	3/5	6/7

Both treated cotton fabric samples have color fastness to rubbing at levels 3-4 and color fastness to light at levels 6-7 (Table 3.16). The color fastness to light of two treated cotton fabric samples is at a high level. This can be explained by the fact that diospyrol in the DM fruit extract and the optimal mixture onto the cotton fabric is easily oxidized by air oxygen and light radiation, making the color of the cotton fabric darker. The color fastness to rubbing of treated cotton fabric samples is quite good, possibly due to the strong influence on the friction force of the testing equipment and the white spirit solvent that reduced the interaction between the organic molecules and the cotton.

3.4.10. Antibacterial ability of treated cotton fabric

3.4.10.1 Antibacterial ability of treated cotton fabric

The results in Figure 3.18 and Table 3.17 show that both rates of killing *S. aureus* and *E. coli* reached 99.9 %. The good antibacterial activity of the two treated cotton fabric samples is due to the antibacterial agents such as Ag-Zn/zeolite, tannins, and flavonoids in the optimal mixture and the DM fruit extract being absorbed on the cotton fabric.

Table 3.17. Antibacterial ability of treated cotton fabric samples

<table>
<tr><th colspan="3">Parameter</th><th>Result</th></tr>
<tr><td rowspan="6">Bacterial reduction rate of cotton fabric treated with DM fruit extract</td><td rowspan="3">E. coli</td><td>0 hour, CFU/sample</td><td>1.8×10^5</td></tr>
<tr><td>24 hours, CFU/sample</td><td>1.0×10^2</td></tr>
<tr><td>% reduction rate</td><td>99.90</td></tr>
<tr><td rowspan="3">S. aureus</td><td>0 hour, CFU/sample</td><td>1.9×10^5</td></tr>
<tr><td>24 hours, CFU/sample</td><td>1.0×10^2</td></tr>
<tr><td>% reduction rate</td><td>99.90</td></tr>
<tr><td rowspan="6">Bacterial reduction rate of cotton fabric treated with optimal mixture</td><td rowspan="3">E. coli</td><td>0 hour, CFU/sample</td><td>1.8×10^5</td></tr>
<tr><td>24 hours, CFU/sample</td><td>1.0×10^2</td></tr>
<tr><td>% reduction rate</td><td>99.99</td></tr>
<tr><td rowspan="3">S. aureus</td><td>0 hour, CFU/sample</td><td>1.8×10^5</td></tr>
<tr><td>24 hours, CFU/sample</td><td>1.0×10^2</td></tr>
<tr><td>% reduction rate</td><td>99.99</td></tr>
</table>

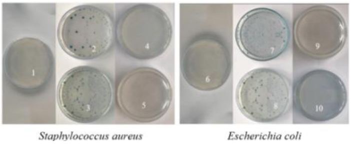


Figure 3.18. Images of agar dishes containing the suspension of treated cotton fabric samples

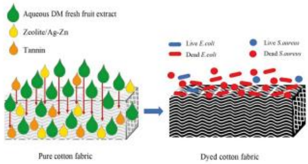
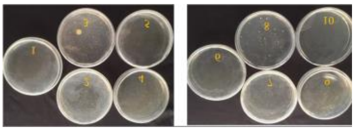


Figure 3.19. Illustration of the antibacterial ability of cotton fabric before and after treatment with the mixture

These agents neutralize enzymes, break down cell walls, and inhibit the growth of bacteria. In particular, the Ag-Zn/zeolite is stable to light and does not decompose, so it is the main ingredient that maintains antibacterial activity for the cotton fabric treated with the optimal mixture. Therefore, the antibacterial cotton fabric treated with the optimal mixture has high potential for application in the medical and textile fields and others.

3.4.10.2. Antibacterial activity of treated cotton fabric after washing

The antibacterial efficiency of the treated cotton fabric samples against *E. coli* and *S. aureus* after washing cycles is presented in Table 3.18 and Figure 3.20.



S. aureus *E. coli*

Figure 3.20. Images of agar dishes containing a suspension of treated cotton fabric samples after 30 washing cycles

Table 3.18. Reduction rate (%) of treated cotton fabric after washing cycles

The washing cycles		**10**	**20**	**30**
Bacterial reduction rate of cotton fabric treated with DM fruit extract (%)	*E. coli*	71.35	56.65	30.33
	S. aureus	71.44	56.79	30.45
Bacterial reduction rate of cotton fabric treated with optimal mixture (%)	*E. coli*	95.05	90.27	85.36
	S. aureus	95.12	90.88	85.78

After 30 washing cycles, the cotton fabric treated with the DM fruit extract can kill 30.33 % and 30.45 % of *E. coli* and *S. aureus*, respectively, reducing by 69.67 %, and 69.55 % compared to the treated cotton fabric before washing. The cotton fabric treated with the optimal mixture has the killing rate of *E. coli* and *S. aureus* bacteria is 85.36%, and 85.78%, respectively, a reduction of 14.63 %, and 14.21 % compared to the cotton fabric treated with the optimal mixture before washing. As the number of washes increases, the antibacterial activity of treated cotton fabric to kill *E. coli* and *S. aureus* bacteria gradually is decreased. The decrease in antibacterial effectiveness over time may be due to the soap solution reacting or interacting with the organic substances on the treated cotton fabric samples as above mentioned. From the obtained results, it is possible to apply cotton fabric treated with the optimal mixture for disposable products such as medical masks, and cotton swabs, or for products that can be used repeatedly such as costumes in the medical field, cotton towels, etc.

3.4.11. Thermal stability of treated cotton fabric

Figures 3.21-3.22 present the TG and DTG diagrams of the untreated and treated cotton fabric samples. As observed from Figure 3.21, the untreated cotton fabric sample lost weight according to one stage with a maximum degradation rate at 368.7 °C (weight loss of 80.51 %). This is mainly due to the breakdown of hydrocarbon linkages in cellulose to form the low molecular compounds (volatile) and charcoal residue (solid part). The charcoal residue at 600 ^{o}C of this sample reached 18.27 %.

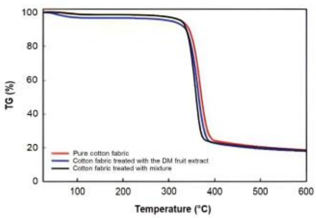


Figure 3.21. TG diagrams of antibacterial-treated cotton fabric samples

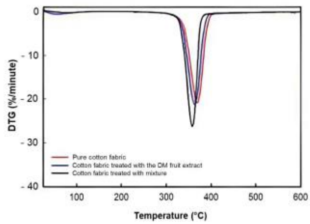


Figure 3.22. DrTG diagrams of antibacterial-treated cotton fabric samples

These results indicate that both untreated and treated cotton fabric samples have high thermal stability. The onset degradation temperature and maximum degradation temperature of the cotton fabric treated with the DM fruit extract are 343.0 ^{o}C and 363.2 °C, respectively. The charcoal residue of the treated cotton fabric sample at 600 ^{o}C is 17.88 %, lower than that of the cotton fabric sample before treatment. This difference may be due to the decomposition of organic compounds treated on cotton fabric at high temperatures.

From Figure 3.21 the cotton fabric treated with the optimal mixture is decomposed strongly when the temperature continuously increases from 300 ^{o}C to 600 ^{o}C. The onset degradation temperature and maximum degradation temperature of this sample are 357.9 ^{o}C and 373.3 °C, respectively.

These values are not significantly different from the cotton fabric sample before treatment. The charcoal residue of the cotton fabric treated with the optimal mixture at 600 ºC is 18.29 %, similar to that of the untreated cotton fabric sample.

From the thermal durability results, it can be seen that the cotton fabric samples treated with the DM fruit extract and the optimal mixture are relatively durable at room temperature and temperatures below 100 ºC. They were strongly decomposed when increasing the temperature above 300 ºC. Therefore, both treated cotton fabric samples should not be used in harsh environments with temperatures higher than 300 ºC.

3.4.12. Formaldehyde and aromatic amine content of treated cotton fabric

3.4.12.1. Aromatic amine content

Table 3.19 reveals that the cotton fabric treated with the optimal mixture does not contain aromatic amines, and meets the requirements of QCVN 01:2017/BCT.

Table 3.19. Prohibited aromatic amines are not presented in textile products

Determined compounds	Compounds		Standard	Result		
	Classification	Code		Sample 1	Sample 2	Sample 3
Azo colorant (mg/kg)	4-Aminobiphenyl	92-67-1	EN 14262-1:2012	ND	ND	ND
	Benzidine	92-87-5		ND	ND	ND
	4-Chloro-o-toluidine	95-69-2		ND	ND	ND
	2-Naphtylamine	91-59-8		ND	ND	ND
	p-Chloroaniline	106-47-8		ND	ND	ND
	2.4- Xylidine	95-68-1		ND	ND	ND
	4,4'-Diaminodiphenylmetan	101-77-9		ND	ND	ND
	3,3'-Diclobenzidine	91-94-1		ND	ND	ND
	3,3'-Dimethoxybenzidine	119-90-4		ND	ND	ND
	3,3'-diclobiphenyl-4.4'-ylendiamin	91-94-1		ND	ND	ND
	3,3'-Dimetylbenzidine	119-93-7		ND	ND	ND
	p-Cresidine	120-71-8		ND	ND	ND
	4,4'-Metylen-bis (2-clo-anilin)	101-14-4		ND	ND	ND
	4,4'-Oxydianiline	101-80-4		ND	ND	ND
	4,4'-Thiodianiline	139-65-1		ND	ND	ND
	o-Toluidine	95-53-4		ND	ND	ND
	2-4-Toluylendiamine	95-80-7		ND	ND	ND
	2,4,5-Trimetylanilin	137-17-7		ND	ND	ND
	o-Aminoazotoluene	97-56-3		ND	ND	ND
	2-Amino-4-nitrotolune	99-55-8		ND	ND	ND
	o-Anisidine(2-methoxyanilin)	90-04-0		ND	ND	ND
	4-Aminoazobenzen	60-09-3		ND	ND	ND
	2.4-Xylidine	87-62-7		ND	ND	ND
	2.6-Xylidine	87-62-7		ND	ND	ND

ND: not determined

3.4.12.2. Formaldehyde content

The results in Table 3.20 show that there is no formaldehyde in the cotton fabric treated with the optimal mixture. According to QCVN 01:2017/BCT, the treated cotton fabric is safe and meets the requirements for textile products for different audiences, including children and infants.

Table 3.20. Formaldehyde content in cotton fabric treated with optimal mixture

No.	Parameter	Standard	Result		
			Sample 1	Sample 2	Sample 3
1	Formaldehyde content (mg/kg)	ISO 14184-1: 2011	ND	ND	ND

ND: not determined

3.5. Evaluate the pollution level of wastewater after the antibacterial treatment process of cotton fabric

From the analysis results of the wastewater parameters in Table 3.21, the BOD values of the wastewater from the treatment process of the cotton fabric with reactive dye, the DM fruit extract, and the optimal mixture increased by 25.16, 11.72, and 11.6 times, respectively compared to the standard value of 50 mg/L. Similarly, the COD values of these wastewater samples also increased by 8.93, 9.45, and 8.9 times, respectively compared to the standard value of 200 mg/L. The TSS value and pH value of the wastewater sample of the treatment process of the cotton fabric with reactive dyes increased by 1.86 times and exceeded the allowable limit by 1.07 times as compared to the standard values. Those values of the wastewater samples of the treatment process of the cotton fabric with the DM fruit extract and the optimal mixture decreased by 0.97 and 0.93 times and remained within the permissible pH range of 5.5 – 9 according to the standard values.

The BOD/COD (B/C) ratios of the wastewater from the treatment process of the cotton fabric with reactive dye, the DM fruit extract, and the optimal mixture reach 0.32, 0.32, and 0.70, respectively. With these B/C values, the wastewater after treatment of the cotton fabric with the DM fruit extract and the optimal mixture will be easier to handle than that after treatment of the cotton fabric with the reactive dye. The high COD content in the wastewater of the treatment process of the cotton fabric with reactive dye can be explained by the incomplete amount of treatment dye on the fabric and the aromatic structure of the reactive dye, leading to difficulty for microorganisms in breaking down the synthetic dye. In contrast, the wastewater after the treatment process of the cotton fabric with the DM fruit extract and the optimal mixture contains easily biodegradable organic substances, resulting in high BOD_5. The lower values of TSS in the wastewater after the treatment process of the cotton fabric with the DM fruit extract and the optimal mixture than that with reactive dye is because the DM fruit extract and the optimal mixture can dissolve in water better than the synthetic dye. Moreover, the impact of ultrasonic, mechanical, and oxidative treatments during the treatment of the cotton fabric also contributed to the reduction in TSS values.

The higher TDS value in the wastewater from cotton fabric processing using reactive dye as compared to that in the wastewater from cotton fabric processing using the DM fruit extract and the optimal mixture is attributed to the significant number of salts such as Na_2SO_3 and auxiliary chemicals used in the treatment process.

From the above analysis, it is possible to apply the biological treatment process for handling the wastewater after the treatment of the cotton fabric with the DM fruit extract and the optimal mixture. It is simple, flexible, low cost, and effective COD removal, availability of biological agents as well as its environmental friendliness. Conversely, wastewater from the treatment of cotton fabric with reactive dye contains residue synthetic dyes that are difficult for microorganisms to degrade, requiring additional chemicals in the treatment process, leading to higher costs and complexity.

Table 3.21. Parameters of wastewater after treatment process of cotton fabric with reactive dye, DM fruit extract, and optimal mixture

Parameters	**Reactive dye (mg/L)**	**DM fruit extract (mg/L)**	**Optimal mixture (mg/L)**	**DOE (mg/L)**
BOD_5	1258	586	580	50
COD	1786	1809	1780	200
TDS	2350	1960	1900	2100
TSS	279	146	140	150
pH	9.5	6	6	5.5 - 9

CONCLUSION

1. The *Diospyrol mollis* (DM) fruit extract has been prepared and the tannin, diospyrol, and saponin content in the DM extract has been determined with values of 9.98 %, 0.12 %, and 16.3 %, respectively.

2. By response surface methodology, the optimal conditions for processing cotton fabric using the DM fruit extract are consist of a temperature of 56.5 ºC, a time of 90 minutes, and a DM fruit extract/water of 89/100 (v/v). The optimal component ratios of the mixture for the treatment of cotton fabric are the DM fruit extract-to-water ratio of 89/100 (v/v), Ag-Zn/zeolite content of 0.083%, and tannin content of 0.085% (the optimal mixture). Cotton fabric treated with the DM fruit extract and with the optimal mixture can kill 99.99 % of two strains of bacteria, *S. aureus* and *E. coli*.

3. After 30 washing cycles with soap solution, the antibacterial effectiveness against *E. coli* and *S. aureus* strains of the cotton fabric treated with the optimal mixture decreased by 14.63% and 14.21%, respectively as compared to the treated cotton fabric sample before washing. The treated cotton fabric still maintains good antibacterial durability.

4. The simultaneous use of the DM fruit extract with Ag-Zn/zeolite and tannin for the treatment of the cotton fabric resulted in high color strength, excellent UV

protection (UPF value of 52.20), high tensile strength and elongation at break, good antibacterial properties, high thermal stability, absence of formaldehyde and prohibited aromatic amines, meeting safety requirements for users (QCVN 01:2017/BCT). The environmentally friendly production process for the treatment of antibacterial cotton fabric contributes to the green trend in the textile industry.

5. Wastewater from the treatment process of the cotton fabric with the DM fruit extract and with the optimal mixture primarily consists of biodegradable organic compounds, which can be easily handled by microbial treatment due to the low BOD/COD ratio. Therefore, the biological treatment of wastewater after treating cotton fabric with the DM fruit extract and with the optimal mixture is simple, flexible, cost-effective due to efficient COD removal, and environmentally friendly. The treated wastewater meets the requirements of QCVN 13-MT:2015/BTNMT.

NOVEL CONTRIBUTIONS OF THE THESIS

1. The extract from the *Diospyrol mollis* (DM) fruits was extracted by using the ultrasonic vibration method combined with the vacuum evaporation method. Tannins, diospyrol, and saponins have been extracted and enriched from the DM extract. The content of tannins, diospyrol, and saponins in the DM extract has been quantified and confirmed the high content of tannins, diospyrol, and saponins in the DM fruit extract.

2. The optimal conditions for the treament process of the cotton fabric with the DM fruit extract have been determined to achieve the ability to kill *E. coli* and *S. aureus* bacteria by 99.9 %. The optimal ratios of the antibacterial treatment mixture for the cotton fabric have been determined with a DM fruit extract/water ratio of 89/100 (v/v), an Ag-Zn/zeolite content of 0.083%, and a tannin content of 0.085%.

3. A process for treating to enhance the antibacterial ability of the cotton fabric has been established using the optimal mixture at the optimal process conditions (a temperature of 56.5 ºC, a time of 90 minutes). The obtained antibacterial cotton fabric can kill 99.99 % of *E. coli* and *S. aureus* bacteria strains and prolong its antibacterial activity. In addition, it has good mechanical properties, is durable to UV rays, has great color fastness to washing, light, and rubbing, and safes for users, and is environmentally friendly.

LIST OF THE PUBLICATIONS RELATED TO THE DISSERTATION

1. **Nguyen, T. T**., Nguyen, C. T., Vo, Q. A., Pham, P. T. H., Thai, H. (2024). Factors affecting dyeing and antibacterial behavior of cotton fabrics dyed with extract of *Diospyrol mollis* Griff, *Cellulose*, 31(2), 1329-1352. (SCIE – IF (2024) = 5.9; Q1).

2. **Trong Tuan Nguyen**, Thuy Chinh Nguyen, Thi Thu Trang Nguyen, Ha Nguyen Manh, Hoang Thai, Comparative study on characteristics and antibacterial capacity of cotton fabrics dyed with reactive dye and *Diospyrol Mollis* extract, *ChemistryOpen*, e202400130, doi.org/10.1002/open.202400130 (SCIE- IF (2024) = 2.3; Q2).

3. **Nguyen Trong Tuan,** Nguyen Thuy Chinh, Nguyen Thi Kim Anh, Nguyen Thi Thu Trang, Trinh Hoang Nghia, Vo An Quan, Vu Manh Hai, Thai Hoang, Assessment of Properties and Antibacterial Ability of Cotton Fabrics Dyed with Optimal Green Dye from Diospyrol Mollis (Griff) Fruits, Tannin, and Zeolite Ag – Zn, *Vietnam Journal of Science and Technology,* (SCOPUS; Q4, accepted for publication, August 23, 2024, doi:10.15625/2525-2518/21102 (2024)).