Enhancement of dye-ability and antibacterial properties of cotton fabrics via modification with chitosan

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Abstract:

Replacement of chemical materials are suitable for modern chemical process. Here; cotton fabrics were treated with chitosan at different concentrations followed by dyeing with acidic dye. The colorimetric properties of the dyed cotton fabrics were evaluated. Also, effects of chitosan concentrations on acid dye uptake were studied. The cotton fabrics which were treated with 3% chitosan produce higher values of K/S, light and washing fastness values. In addition, the chitosan concentration effects on antibacterial activity of the treated cotton fabrics were estimated by using Staphylococcus aureus (S. aureus) as Gram positive bacteria and Escherichia coli (E. coli) as Gram negative bacteria. Results have shown that cotton fabrics treated with chitosan had higher antibacterial properties because of the chitosan properties. Examining with Scanning electron microscope (SEM) confirmed the deposition of chitosan on the surface of cotton fabrics. Durability towards washing and yellowness of both treated and dyed cotton fabrics were also investigated. Therefore, Chitosan was used to enhance cotton fabrics with very good antibacterial activity. In addition to improving its pigment ability with acidic dye.

I was investigated the dye ability of cotton fabrics with acid dye via pre-treatment with chitosan as antibacterial material. To achieve this hypothesis, we treat cotton fabrics with different concentrations of chitosan through pad-dry-cure method followed by dyeing with acid dye. It was found that chitosan enhances the dye ability of cotton fabrics with acid dye to it can create cationic charges from amino groups on the cotton fabrics surfaces. The optimum concentration of chitosan was 3 % (w/v). also colour fastness properties has been enhanced by chitosan and there was slight increase in yellowness and decrease in lightness doe to modification of fabrics with chitosan. Finally, chitosan imparts cotton fabrics also antibacterial activity towards both Gram positive and Gram negative bacteria.

Keywords:

Cotton fabrics, chitosan, Dye-ability, Acid Dyes, Fastness properties, Antibacterial.

الملخص:

استبدال المواد الكيميائية مناسبة للعملية الكيميائية الحديثة. تم هنا معالجة الأقمشة القطنية بالشيتوزان بتركيزات مختلفة متبوعة بالصباغة بالصبغة الحمضية. تم تقييم الخواص اللونية للأقمشة القطنية المصبوغة. أيضا، تمت دراسة تأثير تركيز الشيتوزان على امتصاص الأصباغ الحمضية. تنتج الأقمشة القطنية المعالجة بـ 3٪ من الشيتوزان قيمًا أعلى منK / S ، وقيم ثبات الضوء والغسيل. بالإضافة إلى ذلك، تم تقدير تأثيرات تركيز الشيتوزان على النشاط المضاد للبكتيريا فى الأقمشة القطنية المعالجة باستخدام المكورات العنقودية الذهبية (S. aureus) كبكتيريا إيجابية الجرام و Escherichia coli (E. coli)كبكتيريا سالبة الجرام. أظهرت النتائج أن الأقمشة القطنية المعالجة بالشيتوزان لها خصائص مضادة للجراثيم أعلى بسبب خصائص الشيتوزان. يؤكد المجهر الإلكترونى المسح (SEM) ترسب الشيتوزان على سطح الأقمشة القطنية.

كما تم التحقيق المتانة نحو الغسيل والصفرة من الأقمشة القطنية المعالجة والمصبوغة. لذلک، تم استخدام الشيتوزان لنقل الأقمشة القطنية نشاط مضاد للجراثيم جيد جدا. بالإضافة إلى ذلک ، تحسين قدرتها صبغ مع حمض صبغ. لقد تم التحقيق فى قدرة صبغ الأقمشة القطنية مع صبغة الحمض عن طريق المعالجة المسبقة مع الشيتوزان كمادة مضادة للجراثيم. لتحقيق هذه الفرضية، نتعامل مع الأقمشة القطنية بتركيزات مختلفة من الشيتوزان من خلال طريقة المعالجة بالوسادة الجافة متبوعة بالصباغة بصبغة الحمض. وقد وجد أن الشيتوزان يعزز قدرة صبغة الأقمشة القطنية مع صبغة الحمض لأنه يمكن أن يخلق شحنات موجبة من مجموعات أمينية على أسطح الأقمشة القطنية. وكان التركيز الأمثل للالكيتوسان 3 ٪ (ث / ت). كما تم تحسين خصائص ثبات اللون عن طريق الشيتوزان، وكان هناک زيادة طفيفة فى الصفرة وانخفاض فى ظلال الإضاءة لتعديل الأقمشة باستخدام الشيتوزان. أخيرًا، يضفى الشيتوزان على الأقمشة القطنية أيضًا نشاطًا مضادًا للبكتيريا تجاه كل من البكتيريا الإيجابية الغرام والسالبة فى الجرام.

الكلمات الرئيسية
لأقمشة القطنية، الكيتوزان، قابلية للصباغة، الأصباغ الحمضية، مضاد للجراثيم

1. Introduction

Cotton fabrics have been widely used in textiles industry because of its high contents of cellulose up to 96% according to the fibers weight [1, 2]. The physical and chemical properties of cotton fabrics were excellent, from its stability, water absorptivity, comfortability, and its high affinity towards dyes. Cotton fabrics have high affinity to reactive dyes but it has no affinity towards acid dyes [3] due to its chemical structure which has no basic functional groups. Amination of cotton fabrics has major back draw from its lower degree of substitution and it causes de-polymerization for cotton chains. Therefore, finishing up cotton fabrics with chitosan has great influence on improving its dye ability and enhancing its good antibacterial activity.

Today reactive and direct dyes are widely used for cotton fabrics due to the presence of hydroxyl groups but the main back draw is that cotton fabrics have no affinity towards acidic dyes so that cationic groups were needed to improve the dye ability of cotton fabrics with acidic dyes by using cationized materials for these fabrics.

Although these cationized agents have several advantages for acidic dye-ability of cotton fabrics, we can believe that the chemical process doesn’t fit with environmental aspects regulations because of their toxic effects during the chemical processes [4].

Surface modification of cotton fabrics by using biopolymers such as chitin, chitosan, or gelatin in their finishing processes could offer the best solution to avoid such risks [5, 6].

Chitosan as chitin derivative, which considered the second biopolymer that was presented on earth after cellulose, it is found in crustacean shells, insects exoskeleton and some fungi can produce them from chitin deacetylation [7, 8]. It consists of glucose amine and N-acetyl glucose amine copolymer. Chitosan has several properties such as it is biocompatible, biodegradable and non-toxic, beside it has higher antibacterial properties so that it can be used in many applications especially in textile finishing for many purposes [9, 10].

Textile applications of chitosan can be classified into two main categories: man-made fibers production and fibers wet processing which includes enhancement of both finishing, dyeing and printing processes [11, 12].

Until now most applications of chitosan in textile industries which is considered as antibacterial agent but little applications deal with its role in improvements of dye ability so that our main aim of this study to illustrate the role of chitosan to enhance dye ability of cotton fabrics with acidic dye as well as its antibacterial properties compared with untreated dyed cotton fabrics. [4, 13].

Acid dyes were commonly used for wool and silk fabrics and were rarely used for cotton fabrics due to anionic nature of cotton fabrics. However acid dyes have low affinity towards cotton fabrics. Adding of cationic groups from quaternary ammonium slats has solved these problems but it causes toxicity risks during and after dyeing processes as those are unsafe materials. Therefore, using of chitosan as polycationic biopolymer can solve this problem in addition to producing more safe ecofriendly materials.

The present paper focused on the antibacterial and dyeing properties of cotton fabrics treated with chitosan which is dyed with acidic dyes. Furthermore, other textile properties such as physical and antibacterial activity of the chitosan-finished cotton fabrics were estimated.

2. Materials and Methods

2.1. Materials

Scoured and bleached 100% cotton fabrics were used. Chitosan (CS) (Aldrich, viscosity 1860cps, degree of deacetylation 79.0%). Sodium hydroxide (Modern Lab chemicals), monochloroacetic (Fluka), are used without further purification. Four antibacterial other chemicals and reagents of analytical grade were used without further purification. Antibacterial tests were performed with two types of bacteria: gram-positive bacterium (Staphylococcus aureus, ATCC 1112) and gram-negative bacterium (Escherichia coli, ATCC 11303). These strains were selected because they are the most frequent bacteria in wound infection. Fresh inoculants for antibacterial assessment were prepared on nutrient broth at 37 °C for 24 hours. Acidic dye® (1:2 metal complex) Sunset Blue PA, (C.I. Acid Blue 317), Single azo, OHYOUNG INDUSTRIAL CO., LTD. The structural formulas of dye are shown in Figure 1.

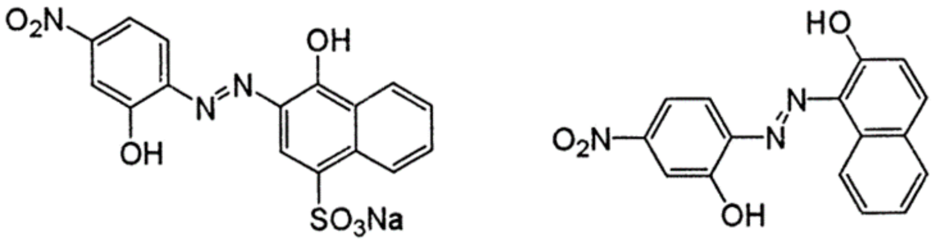


Figure 1. Chemical structure of Sunset Blue PA

2.2. Methods:

Fabric Treatment:

All samples were treated with chitosan by pad-dry-cure method. For this purpose, a 2% (w/v) stock solution of chitosan was prepared by dissolving the required amount of chitosan in an aqueous acetic acid solution at 30˚C for 30-40 min. The cotton fabrics were padded two dips and nips (90–95% wet pick up) in a solution containing chitosan as then immersed directly in aqueous solutions of chitosan (prepared from the stock solution) at room temperature, keeping the material to liquor ratio at 1:30. After treatment, all the fabrics were dried at 100 °C for 5 min and cured at 160 °C for 3 min.

Fabric Dyeing Procedures

The treated and untreated cotton fabrics were dyed with acid dyes by a common process. Where, solution containing 5% dye (o. w. f), and acetic acid with concentration 5% were used. The dyeing process started at 40 °C and raised to 100 °C through 30 minutes and the dyeing was performed at 100 °C for 40-60 min using material-to-liquor ratio 1:50. After dyeing, the fabrics were thoroughly washed with 1-5 g/L of non-ionic detergent for 30 minutes at 60 °C and then were washed with cold water. The dyed fabrics were dried afterwards.

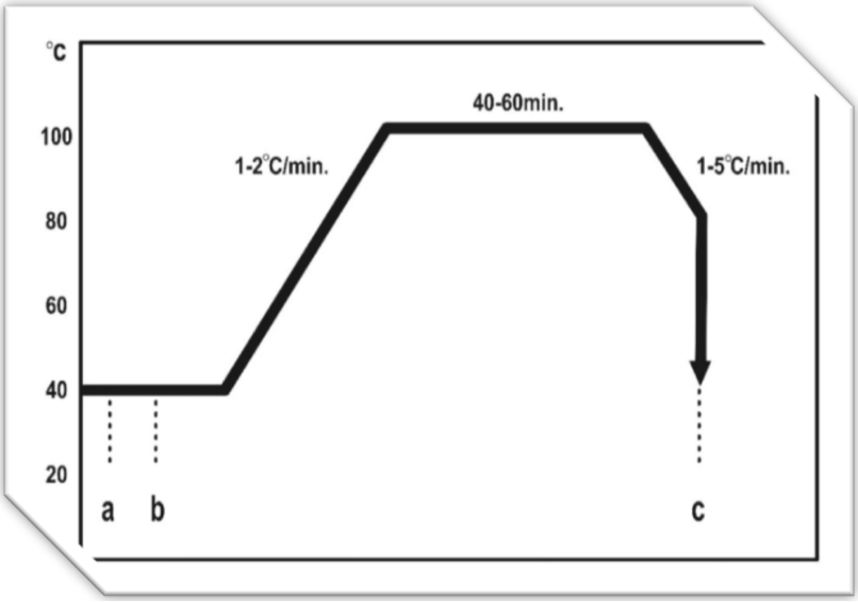


Figure (2) Dyeing curve of Acidic dye.

A: Levelling agent; 0.5-2.0%, PH with Buffer or PH sliding system, B: Dye & C: Drain and Rinse.

Weight add-on was determined after treating the samples with chitosan and dyeing them with reactive dyes and comparing the initial weight (before treatment with chitosan) and final weight (after treatment with chitosan and dyeing) which reported as add-on percentage Eq. (1).

$$\textbf{Weight add} - \textbf{on}\ (\%) = ((\mathbf{W2} - \mathbf{W1})/\mathbf{W1}) * \mathbf{100}$$

Where W1 is the weight of yarn before treatment with chitosan and W2 is the weight of yarn after treatment with chitosan and dyeing.

Fastness Properties:

Washing fastness

Color fastness towards washing was determined according to ISO 105-CO_2:1989 test method [14]. The washing fastness tests were conducted in a launder meter (ATLAS–Germany) using 5g/L nonionic detergent at 50°C for 45minutes. the liquor ratio was 1:50, then the specimen was rinsed with running tap water, squeezed and dried on air. The test specimen and the two adjacent fabrics (cotton and wool) were compared using the gray scale. The rating scale of washing fastness for color change was from 1 (very poor), 2 (poor), 3 (fair), 4 (good) to 5 (excellent).

Light fastness

This test was evaluated according to ISO 105-B02: 1988 test method [15] using a carbon arc lamp. Samples were exposed to a continuous light for 35 hours in order to determine the degree of colour resistance to light photo- degradation. The rating scale of light fastness was from 1 (very poor), 2 (poor), 3 (fair), 4 (moderate), 5 (good), 6 (very good), 7 (excellent), to 8 (outstanding).

Rubbing fastness

Rubbing fastness was determined according to test method ISO 105-X12: 1987 [16] using a crock-meter under conditions for determining dry and wet fastness.

Testing:

Color measurements of the dyed fabrics:

Colour-difference formula ΔE CIE (L*, a*, b*):

The total difference ΔE CIE (L*, a*, b*) was measured using the Hunter-Lab spectrophotometer (model: Hunter Lab DP-9000). The total difference ΔE CIE (L*, a*, b*) between two colours, each given in terms of L*, a*, b* is calculated from:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Where:

ΔE* value: is a measure of the perceived colour size of the colour difference between standard and sample and cannot indicate the nature of that difference.

ΔL* value: indicates any difference in lightness, (+) if sample is lighter than standard, (-) if darker. Δa* & Δb* values: indicate the relative positions in CIELAB space of the sample and the standard, from which some indication of the nature of the difference can be seen.

The colour strength can be calculated as follow:

$$\textit{Relatyive colour strength} = \frac{\textit{K/S of treated sample}}{\textit{K/S of untreated samples}} \times 100$$

Morphology Observation

The surface morphology of undyed and dyed cotton fabrics were investigated by scanning electron microscope (SEM) examination by mounting the samples on stub with double stick adhesive tape and they were coated with gold in a S150A sputter coater unit (Edwards, UK). The gold film thickness was 150 angstroms. The samples were then viewed in a JEOL JXA-950 electron probe micro analyser, Japan.

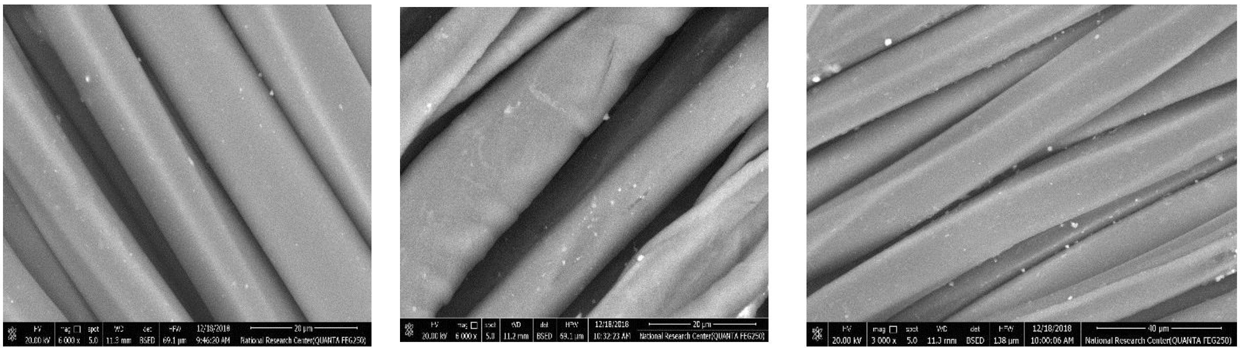
Evaluation of Antibacterial Activity in vitro:

The antibacterial activity of treated and dyed samples was determined against the tested bacteria by disk diffusion method on an agar plate [17, 18]. Briefly, 1 cm diameter blended film samples were cut and put into 10 ml of nutrient agar, to which 10 µl of microbe culture was inoculated, after the solidification. The plates were incubated at 37°C for 24 hours, after which the diameter of inhibition zone were measured and recorded.

3. Results and Discussion:

Morphologies of Silk Yarns

SEM was used to investigate the changes of surface morphology of cotton fabrics. Figure 3 showed these morphological changes through treatment with chitosan and dyeing procedure with acidic dyes. These images confirm the presence of chitosan as foreign substances on cotton fabrics surface compared with blank sample for untreated and undyed cotton fabrics. In addition, the presence of chitosan on cotton surface for rough layer form dyed one.



Untreated and undyed cotton fabrics | **3% chitosan treated undyed cotton fabrics** | **3% chitosan treated dyed cotton fabrics with acidic dye**

Figure 3. SEM images of cotton fabrics through surface modification from treatments and dyeing with acidic dyes

Colour strength:

The K/S value of dyed fabrics was related directly to the amount of dye absorbed at the cotton fabrics by acidic dye. Sunset blue PA acidic dye had higher K/S values as the concertation of chitosan increased as shown in Table 1. This could be attributed to creation of cationic site on cotton fabrics that increased as the amount of chitosan increased on the cotton fabrics.

Chitosan has three reactive groups; one amino group and two hydroxyl groups (one group is primary and the other is a secondary group), can bind with fabrics and acid dye at the same time with and without crosslinking agent.

Table 1. Effect of chitosan concentration on colour strength of acid dye:

Chitosan concentration (%)	K/S	ΔE	Relative colour strength
0	1.03	31.50	100
0.5	1.98	33.23	192.23
1.0	2.12	34.05	205.82
1.5	2.32	35.65	225.24
2.0	2.5	38.56	242.71
2.5	2.98	41.62	289.32
3.0	4.03	43.52	391.26
3.5	3.89	42.25	377.66
4.0	3.76	40.90	365.04
4.5	3.64	37.68	353.39
5.0	2.91	35016	

Also we can have an observation that K/S values have increased as the chitosan concentration increased up to 3 wt.% and after that it decreased. The reason is because concentration the cotton fabrics became saturated with chitosan and do not need any of that for dyes. While it will be competing the fabrics for dye absorption which gave that decrease in K/S values after that concentration.

Also the energy difference shows the same trend like K/S for chitosan concentration which has significant increase until 3 wt. % chitosan concentration after that it will be decreased for the same reason.

Fastness Properties

The dyed cotton fabrics with shade 2%, were subjected to washing with 2 g/L nonionic detergent at 88 ^{o}C for 0.5 h, and light to investigate their durability towards light and washing. Table 2 illustrates fastness properties towards washing, rubbing and respiration of chitosan treated cotton fabrics dyed with acidic dye.

Table 2: fastness properties of acidic dye on chitosan treated cotton fiber

Chitosan concentration	Fastness to rubbing		Wash fastness**			Fastness to perspiration**						Light
						Alkaline			Acidic			
	Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
1.0	4-5 4-5	4 4	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5
3.0	4-5 4-5	4 4	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	5
5.0	4-5 4-5	4 4	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	4-5 4-5	5-6

*** C, Cotton; W, wool; S, silk; **Alt = alteration; SC = staining on cotton; SW = staining on wool**

Colour Change

Table 3 illustrates the colour change of cotton fabrics treated with different concentrations of chitosan. It could be showed that yellowness of treated cotton fabrics increases as the concentration of chitosan increases (b* values) whereas there was slight decrease in lightness of these fabrics as chitosan concentrations increased (L*) values. This is because amino groups of chitosan can react with hydroxyl groups in cotton fabrics. Therefore, the cotton fabric lusters aren’t changing as chitosan concentration increased.

Table 3 colour change of cotton fabrics treated with chitosan at different concentrations:

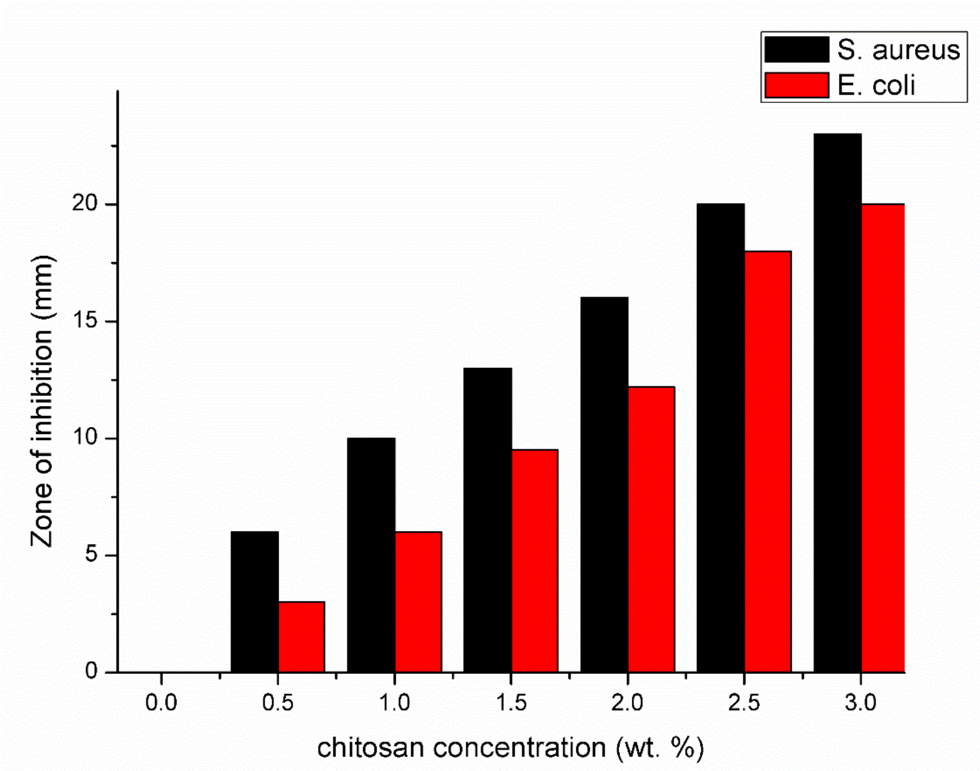
Chitosan concentration	L*	a*	b*
0	65.16	-0.665	4.46
0.1	64.32	-1.65	5.32
0.2	64.23	-0.98	5.65
0.5	63.98	-1.605	5.98
1	63.62	-1.261	6.23
3	63.58	-0.984	6.81
5	65.09	-1.230	4.99

Anitbacterial Activity:

Cotton fabrics were investigated for its antibacterial activity in several forms in chitosan treatment and dyeing with acid dyes.

Figures 4 and 5 illustrates the antibacterial activity of treated and dyed cotton fabrics towards S. aureus as Gram positive and E. coli as Gram negative bacteria. In general, the antibacterial activity expressed in zone of inhibition was increased as chitosan percent increased towards both Gram positive and Gram negative bacteria do to some type of reaction of amino groups of chitosan that carry positive charges with bacterial cell wall that has negative charges.

In addition, we could see that the antibacterial activity of these treated dyed fabrics had more efficiency towards Gram positive bacteria than Gram negative bacteria due to bacterial structure difference of the outer layers of cell walls from Gram positive that have more open free structure than that of Gram negative that had more tight closed outer cell wall.



4. Conclusion:

I investigated the dye ability of cotton fabrics with acidic dye via pre-treatment with chitosan as antibacterial material. To achieve this hypothesis, we treat cotton fabrics with different concentrations of chitosan through pad-dry-cure method followed by dyeing with acidic dye. It was found that chitosan enhances the dye ability of cotton fabrics with acidic dye, it can create cationic charges from amino groups on the cotton fabrics surfaces. The optimum concentration of chitosan was 3 % (w/v), also color fastness properties have been enhanced by chitosan and there was slight increase in yellowness and decrease in lightness de to modification of fabrics with chitosan. Finally, chitosan imparts cotton fabrics also antibacterial activity towards both Gram positive and Gram negative bacteria.

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