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Printed Cotton Fabrics with Antibacterial Properties Based on Honey Gum Containing Printing Paste Formulation

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PROPOLIS is a gum has been used as a traditional cure for various diseases due to a variety of biological activities of this folk medicine. In the present work, an attempt made to investigate antibacterial printed cotton fabrics using different concentrations of propolis inside printing paste formulation. The interaction between printing paste containing propolis and cotton was confirmed using FTIR. Morphological properties and printing pigment distribution were examined using SEM. Printing color strength and fastness properties were examined. Antibacterial activity was explored against gram positive, negative and yeast. ATR/IR showed different intensities at OH region that confirm interaction between propolis and fabrics and in comparison with fabric and printed cotton without propolis. Thick coating and highly distributed fabrics were visualized at SEM images at printed cotton fabrics containing propolis. The color strength of printed cotton fabrics containing propolis was directly proportional with propolis content up to 4%. Printed cotton fabrics containing propolis showed stability at all fastness evaluations. Printed cotton fabrics containing 4% propolis showed efficient antimicrobial activity towards both gram positive and negative bacteria

Keywords: Propolis, Cotton fabrics, Pigment dye, Printing, Antibacterial activity, Thermo-fixation.

Introduction

The wide usage of textile is assuming the responsibility to answer costumer's updated needs and aspirations. Now days', textiles not only utilized for covering applications, but also used for protecting, treating and diagnosing as well. To achieve this goal, many scientists' interest by introducing some materials was not used in textile industry before such as nano-metallic particles [1-4], natural materials as chitosan [5-7] and propolis [8].

Propolis is a gum collects by honey bees from various plants; the honey bees use propolis to seal holes in their honey combs, smooth out the internal wall and protect the entrance against intruders. Bees use resinous material called Propolis (bee resin) for sealing cracks and gaps in the hive (beeswax seals the larger gaps). Propolis composed water and ehanolic extracts beside volatile oils. Main components of ethanolic extract are flavonoids and polyphenolic acid, while water extract constituents include phenolic acids, caffeoylquinic acid, 3-mono- caffeoylquinic acid caffeic acid, flavonoids, etc. As a natural mixture, propolis is widely used in medicine, cosmetics and food. So far, various attempts have been made to make use of propolis in the textile finishing but not at printing process.

As a result of propolis astonishing composition, many researchers have tested propolis against several dangerous microbes, and the results suggest that propolis is powerful against aggressive bacteria. Although the strength of propolis can vary based on geography, its protective benefits remain constantly present. Part of the reason for the action may be due to it containing a wide spectrum of flavonoids [9]. Moreover, Researchers have determined that

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propolis offers powerful antibiotic properties. The isolated acids from propolis have been shown to be an effective agent against many bacteria, including staph [10]. In one study, Brazilian propolis was tested against a common prescription cream used to help burns. The results, the propolis was just as effective. Propolis was even more soothing for minor burns than the conventional medication [11, 12]. For diabetes, studies have shown that propolis may inhibit enzymes that increase blood sugar [13, 14]. It is believed that the antioxidant compounds in propolis are responsible for their blood sugar-stabilizing benefits.

Textile process divided into various wetting process assizing, scouring, finishing, dying and printing. Unfortunately, textile processing consumes a high amount of water and energy, besides negative impact on environment. Many efforts spent to overcome this weak point. The combination between two wetting process of textile industry steps as bleaching and scouring for example save money, energy and ecofriendly.

Our group previously used ZnO NPs previously prepared by sol-gel inside printing past producing high stable printed fabrics with antibacterial property. Not only Propolis used for producing antibacterial textiles as a result of its constituent, but also increases physical properties as tensile strength at high temperature. Water extraction propolis (WEP) showed a crosslinking behavior at high temperature [8]. From this point, these results inspire us to add propolis to the printing paste that will produce antibacterial printed fabrics besides scavenging properties and crosslinking at fixation process that suspect positive impact on color strength properties.

Current work deals a new application of propolis (as antibacterial agent) in textile printing. According to the author's background, no work has been published in this field. Propolis was applied on pigment printing paste to prepare antibacterial textile prints. The produced prints evaluate through color strength, fastness properties (light, washing and rubbing) and antibacterial activity.

Materials and Methods

Materials

Propolis: Egyptian propolis samples were collected from farm in Giza, Cairo, Egypt.

Fabrics

Mill – desized, boiled bleached poplin cotton fabrics produced by Misr Helwan for spinning Co., Cairo, Egypt. Green 3 Gl as a pigment dye is kindly supplied by Daico for chemicals industry S.A.E.Synthetic thickener, Dais thick was kindly supplied by Daico Company, Cairo, Egypt. Binder DBIt was kindly supplied by Daico Company, Cairo, Egypt.Urea and Diammonium phosphates and all other chemical are laboratory grade.

Methods

Printing

The paste used for application of pigment in printing cotton fabric was prepared as appear at Table 1, All printing pastes were applied to 100% cotton fabrics using the á conventional screen-printing technique. Prints were dried at room temperature, and then fixated at 150 °C for 4 min in an automatic thermo fixation oven (WemerMattris Co., Switzerland). Printing was carried out by the conventional screen-printing technique. Samples printed with the prepared printing pastes containing pigment dye with and without propolis were first dried then fixated by thermo-fixation technique at150°C for 4minutes. The fixation of dye on the fabric carried out at atmospheric pressure.

While X Propolis means (0, 1, 2, 3, 4 and 5) and Y water means the complementary volume to reach one liter

Washing

Washing process of the prints was carried out through four stages: 1) thoroughly with cold water, 2) washing with hot water, 3) soaping using 2g/l non-ionic detergent namely Espycon 1030 at 90-95 °C for 15 minutes, and 4) washing with hot water. The samples were dried and assessed for color strength and overall fastness properties.

Testing and analysis

ATR/IR (Jasco infrared system):

JASCO INFRARED SYSTEM spectroscopes equipped with an ATR were used to record and analyze the blank and modified textile samples. A total of 30 accumulative scans were taken per sample with a resolution of 4 cm^{-1}, in the frequency range of 4000–400 cm^{-1}, in the transmission mode.

Scanning electron microscopy (SEM)

This was studied using a scanning electron probe microanalyzer (type JXA-840A) – Japan Scanning electron microscopy (SEM). It was used to detect the changes in surface characteristics of the cotton fabrics due to the treatment with propolis.

Color strength (K/S) and fastness properties

The color strength of the printed samples expressed as K/S at the same time and after storing the printing paste for 3 and 5 days.

The overall fastness properties (washing, perspiration and rubbing) were assessed according to standard methods [15, 16].

Antibacterial activity

The antibacterial activity of the untreated and treated printed samples against *Staphylococcus aureus (G +ve) and Escherichia coli (G−ve)* bacteria were determined using agar plate. The plates were incubated at 37◦C for 24 h a growth free zone of inhibition around the fabric appears as antibacterial agent migrates from the fabric onto the agar and diffuses outward. Diameter of inhibition zone was determined according to AATCC test method 100-199.

Results and Discussions

ATR/IR (Jasco Infrared System)

Figure 3 represents ATR/IR chart for cotton fabric printed cotton fabric with and without propolis. Cotton fabrics peaks represent at Fig 1a, a peak at 3500 represent to hydroxyl groups (OH) of glycoside ring, while peak at 1010 cm-1 represents to C-O-C ether linkage. Further, peak at 2930 represents to alkyl ethylene groups. For the printed cotton fabrics, it seems decline at hydroxyl group intensity that may represent intercalation between cotton fabrics and printing past. In addition, new peaks found at 1650 cmi1 and peak 1638 cm−1 may be attributed to carboxylate groups exhibited at printing past formulation as acrylate groups belong to binders and carbonyl group belongs to urea. Alternatively, hydroxyl group of cotton fabrics treated with printing paste containing propolis showed ascending intensity of OH at 3500 cm-1, this may attributed to the propolis composition of flavonoids and enhanced and new carboxylic peaks attributed to phenolic acids containing propolis. In comparison with ATR of Hebeish et al; propolis showed high intensity peak compared with printed cotton fabrics containing propolis, it may attributed to crosslinking theory of propolis molecules via ether linkage with cellulose chains at high temperature as suggested at Fig. 3 [8].

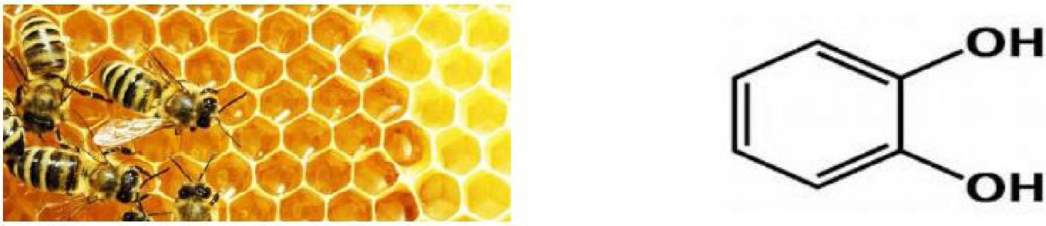
Scanning electron microscopy (SEM)

The SEM images (Fig. 3a, b, c) show the surface morphology of untreated and treated printed cotton fabric with propolis respectively. Fig. 4a shows the cotton fibers crystalline and amorphous regions. Its known that glycoside rings of cotton fabrics containing crystalline regions as result of homogenous distribution of ether linkage units, while amorphous regions attributed to hydrogen bonding between hydroxyl groups containing glycoside chains. Fig. 3b belongs to cotton fabrics containing printing paste, showed a coating layer and shining particles. It may attributed to high viscous printing paste that containing binder and shining particles represent salts containing printing paste as urea. Fig. 3c showed cotton printed fabrics containing propolis. It's clear (Fig. 2c) that the treated printed cotton containing propolis fabric sample exhibited denser layer filling interspace than printed cotton. As mentioned before, Propolis can interact with both cotton fabric and printing past that visually increased the viscosity of the printing past which reflects on density of printing past.

Effect of propolis concentrations on Color strength (K/S) and fastness properties of printed fabrics

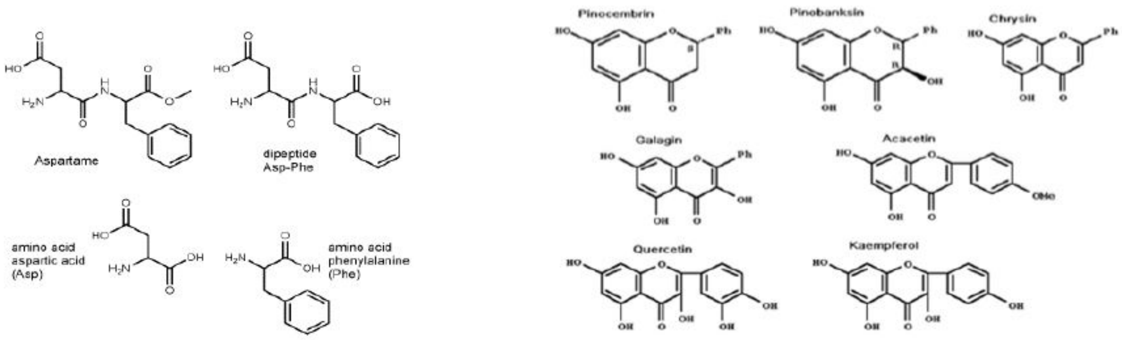
All printing pastes were applied to 100% cotton fabrics using the conventional screen-printing technique [17] at the same time and after storing the printing paste for 3 and 5 days. Table 2 and Fig 4 showed the effect of propolis concentrations (1-5%) on color strength of the printed cotton fabrics (K/S), the printing process was carried out in presence of synthetic thickener in printing paste and thermo fixation. From the figures, 'it is clear that color strength value of printed cotton fabrics increases until 18.73, 17.43 and16.29 respectively for the same time 0, 3 and 5 days by increasing propolis concentration at pigment printing paste up to 4%, after this concentration K/S value decrease.

The increase of color strength may be attributed to physical and chemical properties of propolis. For physical issue; propolis as brown color material, its mixture with another colored material will increase the RGB properties which reflect positively on color strength ascending k/s results. While the chemical issue; the chemical composition of propolis that act as self crosslinker with cotton fabric and printing past, CAPE in previous study showed enhancement at crosslinking efficiency appears clearly at mechanical properties. In other meaning, more crosslinking results from propolis with cotton



Honey comb **Phenolicacid**

Fig. 1. Structure of Propolis



Pollen

Flavonoids in Propolis

Fig. 2. Chemical constituents of propolis.

TABLE 1. The printing past formulas for producing propolis containing printing pastes.

Pigment dye	40 gm
Binder	100 gm
Diammonium phosphate	25 gm
thickner	600 gm
Urea	40 gm
Propolis	X
Water	Y

fabric assist scavenging printing past inside cotton fabrics that increases the color strength properties.

The decrement appears after increasing to 5%, it may attributed to high crosslinking between cotton fabric and propolis that act as a barrier of past penetration inside the fiber. Another reason, increasing propolis percent over 4% may increase the viscosity to limit the penetration process inside cotton fiber. Besides, increasing percent of brown color of propolis may affect negatively over 4% of propolis inside printing paste. Another interpretation, Hydrogen bond formation between phenolic and flavonoids compounds in propolis and hydroxyl group in cotton fabrics and combination between anionic and cationic groups in amino groups of in protein molecule in propolis compounds and cotton fabrics. This is leading to increasing in color strength of the printed cotton fabrics (K/S) due to migration dye to the printed surface after fixation. It is clear that all fastness properties of the printed cotton fabrics, prints were between very good and excellent. After storing of printed cotton fabrics, there is no significant effect on color strength (K/S) and overall fastness properties as it is evident in Table 2.

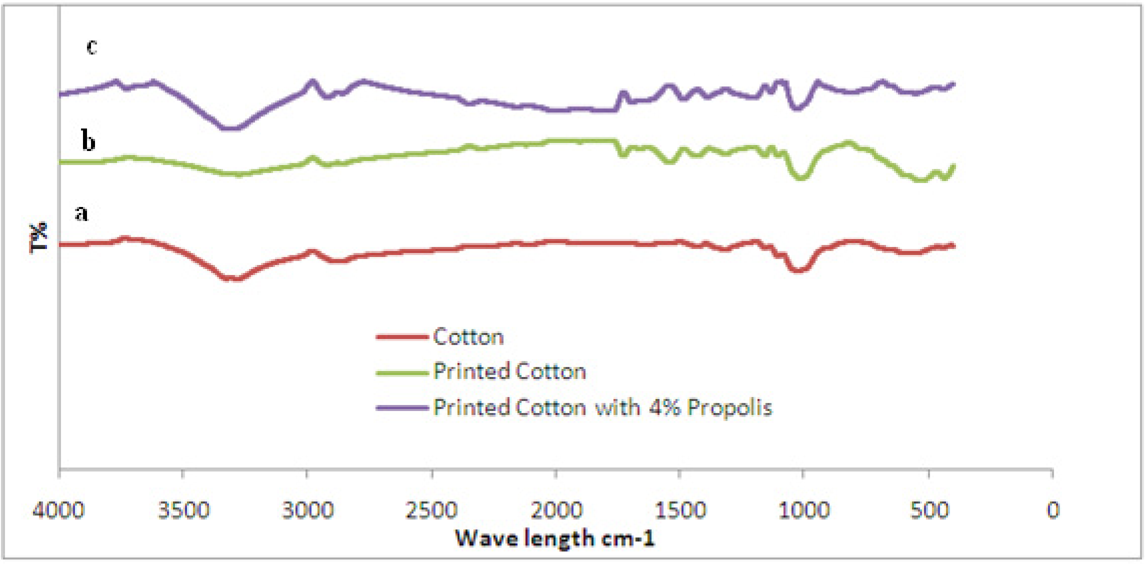


Fig. 3. ATR/IR of a) cotton, b) Printed cotton and c) printed cotton containing 4% propolis.

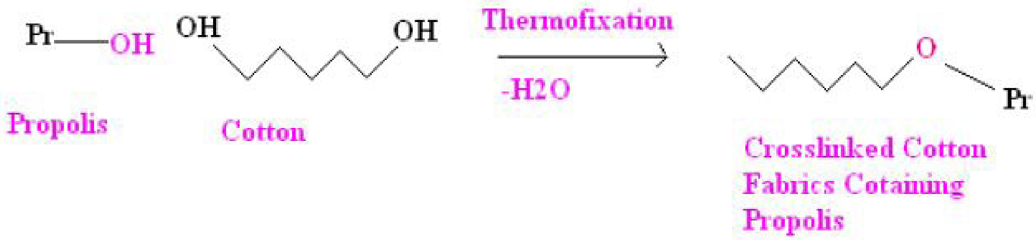


Fig. 4. Crosslinking mechanism of propolis and cotton fabrics

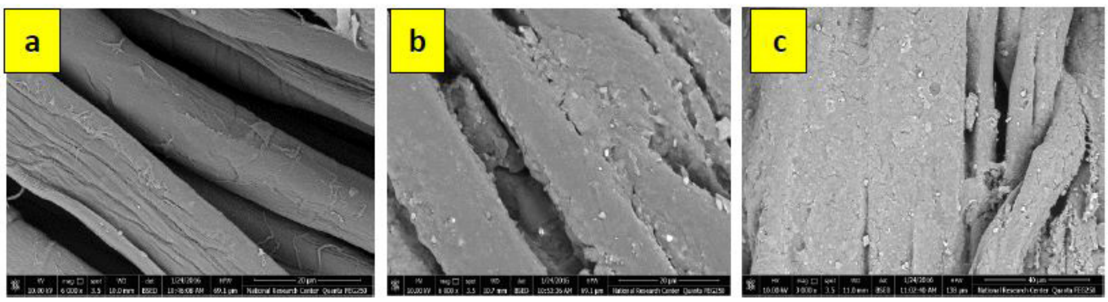


Fig. 5. The SEM images of untreated and treated printed cotton fabric with propolis

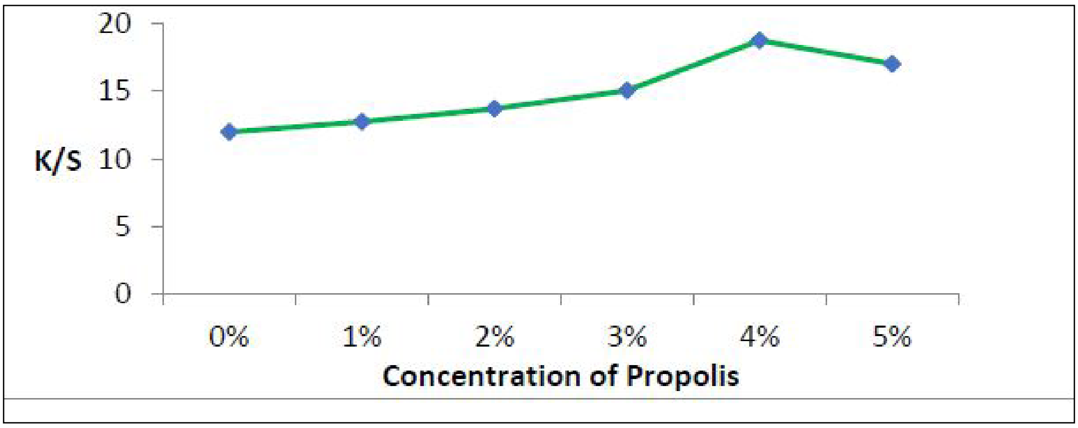


Fig. 6. Effect of propolis concentrations on Color strength (K/S).

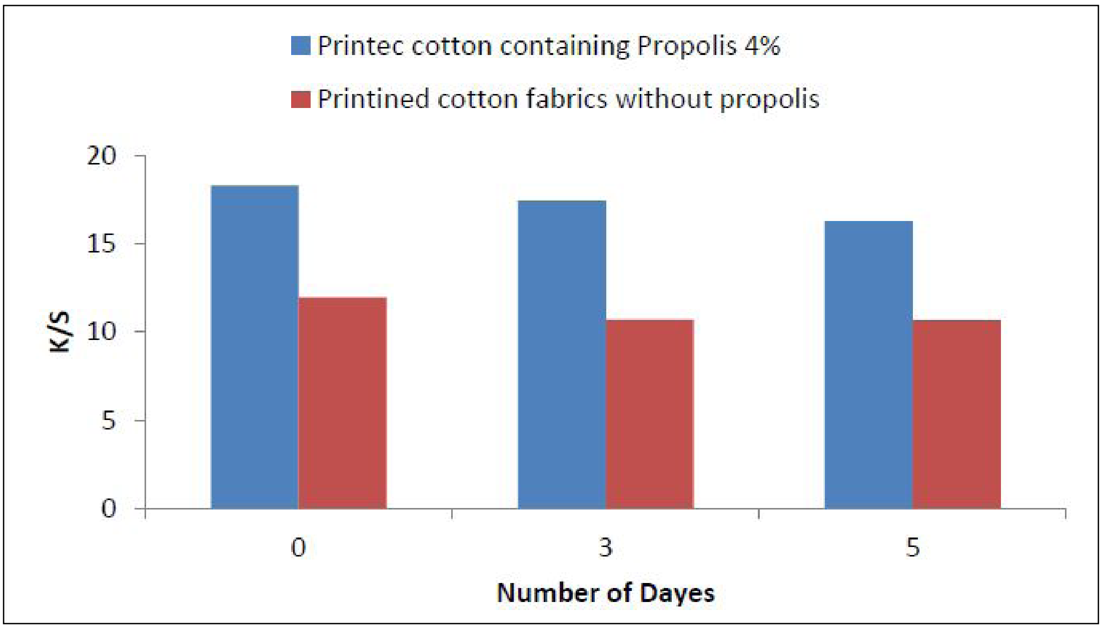


Fig. 7. the effect of Storing days of printed cotton fabrics containing 4% propolis on color strength.

Effect of Storing days on printed cotton fabrics containing 4% propolis on color strength.

Table 2 and Fig. 5 shows the effect of storing time on color strength of printed cotton fabrics containing 4% propolis at 3 days and 5 days. There is no marginal decline in color strength. The color strength of printed cotton fabrics containing propolis still high in case of comparing with the printed cotton fabric without propolis. It's also obvious that the decline of color strength appears clearly for all samples either printed in presence or absence of propolis.

Effect of propolis concentrations on fastness properties

The printed cotton fabrics showed a stability at all fastness examinations (washing fastness, Rubbing fastness, Perspiration fastness and light fastness) compared to printed fabrics without propolis. Whatever the percent used at printing paste formulation, it showed same stability. Interestingly, rubbing fastness (Table 2), showed directly proportional results with propolis concentration inside printing paste. As known, rubbing properties reflects the printing past adhesion to fabric after exposing to harsh mechanical pilling. It's clear from Table 3 that

TABLE 2. Effect of propolis concentration on overall fastness properties of printed fabrics

N days	substrate	k/s	Washing fastness		Rubbing fastness		Perspiration fastness				Light fastness
							Acidic		Basic		
			Alt.	St.	Dry	Wet	Alt.	St.	Alt.	St.	
0 day	without Pr	11.98	4	4	4	3	4-5	4-5	4-5	4-5	7
	1%	12.73	4	4	4.5	4	4-5	4-5	4-5	4-5	7
	2%	13.7	4	4	4.5	4	4-5	4-5	4-5	4-5	7
	3%	15.54	4	4	4.5	4	4-5	4-5	4-5	4-5	7
	4%	18.73	4	4	4	4	4-5	4-5	4-5	4-5	7
	5%	17	4	4	4	3-4	4-5	4-5	4-5	4-5	7
3 days	without Pr	10.72	4	4	3-4	3-4	4-5	4-5	4-5	4-5	7
	1%	12.69	4	4	4	4	4-5	4-5	4-5	4-5	7
	2%	12.84	4	4	4	4	4-5	4-5	4-5	4-5	7
	3%	15.40	4	4	4	4	4-5	4-5	4-5	4-5	7
	4%	17.43	4	4	4	3	4-5	4-5	4-5	4-5	7
	5%	16.87	4	4	4	4	4-5	4-5	4-5	4-5	7
5 days	without Pr	10.7	4	4	4	3	4-5	4-5	4-5	4-5	7
	1%	12.52	4	4	4	3	4-5	4-5	4-5	4-5	7
	2%	12.47	4	4	4	3-4	4-5	4-5	4-5	4-5	7
	3%	15.11	4	4	4	3	4	4-5	4-5	4-5	7
	4%	16.29	4	4	4	3-4	4	4-5	4-5	4-5	7
	5%	14.46	4	4	4	4	4	4-5	4-5	4-5	7

TABLE. 3. Antibacterial activity of cotton fabric, printed cotton fabrics with and without 4% propolis.

Sample	Cotton Fabric	Printed cotton	Printed cotton containing 4% Propolis
E.Coli	--	---	10 mm
Staph. Auraus	--	--	10 mm
Speragelisniger	---	---	15 mm

printed cotton samples containing propolis showed rubbing properties over printed cotton without propolis, it may attributed to additional crosslinking property resulted from interaction between printing paste and cotton fabric in presence of propolis.

Microbiological evaluation of printed fabrics with and without propolis

The microbiological evaluation of propolis represent in Table 3 showed that blank and printed cotton fabrics haven't any microbiological resistance towards either bacteria or yeast. The cotton composition of glycoside chains act as feeding for microbes that assist its growth. While printed fabrics containing propolis showed low antibacterial activity and high antifungal properties. "CAPE" as a potent antibacterial agent exhibited at Propolis beside flavonoids and phenolic ester affects positively on antibacterial activity.

Conclusion

New printing cotton fabrics with antibacterial activity successfully prepared based on printing paste containing propolis. The attachment between propolis and cotton fabrics and its efficient at scavenging printing pigment was confirmed using FTIR. SEM showed distribution of printing paste as enhancing viscosity of propolis filler. Printing cotton fabrics containing propolis showed high color strength up to 4% and stable fastness properties. Printed cotton fabrics containing 4% propolis showed efficient antibacterial properties towards gram positive and negative bacteria compared to cotton fabric and printed cotton fabrics without propolis.

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