Egypt.J.Chem. **Vol. 62**, No. 5. pp. 1261 - 1267 (2019)

Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Antibacterial Treatment of Cotton Fabrics Using Methy Lisothiazolinone

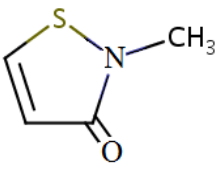
M.F. Shaaban* and A. S. Montaser
Textile Research Division, National Research Centre, Dokki, Giza, Egypt.

THE prevailing study is an strive to utilize methylisothiazolinone (MIT) which was applied efficiently in other applications away from fabric finishing fields such as preservation and health care. Different concentrations of the substance were applied to the scoured woven cotton fabric, the use of distinct methods of treatment which includes Exhaustion and pad-dry-thermo-fixation. The results obtained showed that using pad-dry-thermo-fixation gave better anti-bacterial conduct more than the exhaustion method. Furthermore, by varying the different factors influencing the reaction such as MIT's concentration (10-50 mg/l or ppm), curing time (1-10 min.) and curing temperature (120-170°C) the study reached the optimum conditions to get the best anti-bacterial treatment for cotton fabrics against gram positive bacteria(*Staphylococcus Auras)* and gram negative bacteria (*Escherichia Coli*) . FT-IR spectroscopy, Antibacterial test according to (AATCC) and SEM were used to assure the obtained results.

Keywords: Antibacterial activity, Cotton, Finishing and Methylisothiazolinone.

Introduction

Methylisothiazolinone, (MIT) (now and then mistakenly called methylisothiazolinone), is a ground-breaking engineered biocide and preservative within the series of isothiazolinones, which is utilized in various individual care products and an extensive variety of industrial applications like slimicides in cooling tower used in Electrical power stations and other applications[1-2]. It is a cytotoxic that may influence diverse sorts of cells. Its utilization for an extensive variety of personal products for humans, for example, beauty care products, salves, creams, sterile wipes, shampoos, and sunscreens, dramatically expanded amid the primary decade of the twenty-first century and has been accounted for as a contact sprucing operator by the ecu fee's clinical Committee on client protection[3].



Methylisothiazolinone

Industrial applications are also quite extensive ranging, from preservative and sanitizing uses to antimicrobial sellers, power production, additionally, it's far employed as preservatives for growing the shelf life of paints in cans via stopping the growth of molds and fungus [4]. it is also used in family and business merchandise such as, metal operating fluids, paper mills, reducing oils and jet heating fuels [5], because it has been observed to show off organic interest in the direction of a number of micro-organisms. Metalworking fluids, mining, paint manufacturing, and paper manufacturing, lots of which boom potential publicity to it by using humans in addition to organisms, each terrestrial and marine.[6].

Measurements of CMI/MIT concentrations in air samples of freshly painted rooms have shown that their concentrations after a few days may nonetheless be excessive enough to elicit airborne reactions in patients. The general public health authorities have therefore raised issues on the harmful aspect results of isothiazolinones. The decomposition of isothiazolin-3-ones is now turning into a vast mission to environmental

*Corresponding author e-mail: drmohamed727@gmail.com
Received 30/11/2018; Accepted 26/12/2018
DOI :10.21608/ejchem.2018.6447.1544

chemists, considering the fact that: (1) its biodegradation is typically very gradual requiring numerous days or perhaps weeks; (2) the continuing growth within the manufacturing and intake of these products [7]; and (3) the multiplied client resistance towards this chemical, due to the allergies it may cause in people, while uncovered to freshly painted interiors. There is a developing demand for effective, economic and environment pleasant treatment technologies, wherein all of the materials used (or produced) are mineralized to absolutely harmless products. Therefore, a paint which on software can activate a photocatalytic procedure and wreck the isothiazolin-3-ones within a totally short time, will be appealing to clients and healthcare inspectors.

The aim of this work is to utilize MIT to cotton fabrics to enhance their antibacterial performance, followed by some important tests to assure its influence.

Experimental

Material

Cotton: Mill desized, scoured and bleached cotton fabric (130 g/m2) produced by El-Nasr for Spinning and Weaving Company, Mehala, Egypt.

Chemicals

Methylisothiazolinone (MIT) was purchased from Rohm and Haas Research Laboratories, Spring House, PA, USA, Acetic acid, Caustic soda and other chemicals are all of lab. Grade is delivered from ADWIC Co, Egypt.

Treatment Procedures

Exhaustion Method

Where 1 g samples of cotton fabrics where treated with a certain concentration of MIT (1% o.w.f) using liquor ratio 1:20 at ambient temperature for 1 hour using shacking water bath. Then dried at 100 °C for 2 min., then cured at 120°C for 1 min. then N% content was measured for the sample.

Padding Method

Where 1 g samples of cotton fabric were socked in a certain concentration of MIT (10 mg/l i.e. 10 ppm) using a padding machine (Matisse-Switzerland) with a pick up 100%, then dried at 100 °C for 2 min., then cured at 120°C for 1 min. then N% content was measured for the sample.

Instrumental analysis

SEM- Macrograph

The surface morphologies of the functionalized cottons at various stages were characterized by using a JEOL JSM 840A (Tokyo, Japan), Scanning Electron Microscope (SEM) at an accelerating voltage of 15 KV.

N% Content

It was measured according to Kjldahle's method. The following equation was used to calculate the nitrogen content on sample weight (Wt.) [8].

$$\text{Nitrogen Content (\%)} = \frac{0.014 \times N \times V \times 100}{Wt}$$

Where N is the normality of hydrochloric acid used for titration, Wt. is the weight of fabric.

FT-IR spectroscopy

Measurements were performed using Nexus 670-FTIR spectrometer Nicolet USA at the range of 4000-400 Cm^{-1} and a resolution of 4 Cm^{-1}.

Antibacterial Activity

To evaluate the antibacterial activity for gram positive bacteria(*Staphylococcus Auras)* and gram negative bacteria (*Escherichia Coli*), we used (ATCC 6538) and (AATCC 147:2008) methods. Four samples named S1-S4 each contains 0.5 gm. of sterilized sample mixed with 100 ml of 106 CFL/ml bacteria solution respectively. Putting the mixture in a conical flask and cultured in a shaker incubator at 37°C for 24 hrs. With 120 rpm. S1 used as the control sample, where S2-S4 considered the test samples. We diluted the bacteria culture solutions by a factor of 104 using the ten-time dilution method, then, 1 ml of each diluted bacterial solutions mixed with 15 ml nutrient agar and placed into Petri dishes. After mixing and coagulation the samples cultured at 37°C for 24 hrs., the colony count on the plate then calculated using the following formula:[9]

Percentage of viable Cell= K/K_0

Where K_0 is the control colony count and K is S2-S4 colony count.

Results and Discussion

Effect of Treatment Method used on N% content

Using padding technique where a 1 gram cotton sample was impregnated in the MIT solution (10 ppm) using a Padder to squeeze the sample at 1 bar pressure with a pick up 100%, then drying at 100°C for 2 min. followed by curing at 120°C for 1 min., gave better nitrogen content percent more than the exhaustion method where 1 gram of cotton fabric sample was put in a conical flask (1% o.w.f) using

shaking water bath at ambient temperature for 1 hour, then dried at 100°C for 2 min. followed by curing at (120-170°C) for time (1-5 min.). The results as shown in Fig. 1 showed that using padding technique affords better results than exhaustion method this is may be ascribed to the fact that using pressure in the padding technique will enable greater quantity of MIT to be trapped into the cotton lattice more that occurred in the exhaustion method [10].

Effect of MIT concentration

Figure 2 illustrates that on using padding technique using different concentration of MIT (10-50 ppm) and curing at 120°C for 1 min. the more the MIT concentration the greater the N% content up to 50 ppm, but beyond 50 ppm some allergy effect may be take place, and to avoid the allergic effect on the cotton treated fabrics we stopped our study on using 50 ppm. The increment in the N content will be associated with the quantity of MIT containing N atom.

Effect of Curing Time

Figure 3 shows that by using padding technique where the MIT concentration is 50 ppm, curing temperature 120° C for different time (1-5 min.), the N% content increases up to 3 minutes and it decreases afterwards. This may be attributed to the fact that, beyond that time a partial thermal

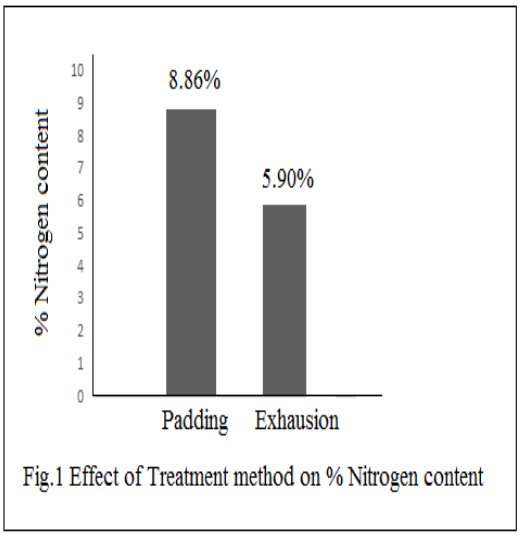


Fig.1 Effect of Treatment method on % Nitrogen content

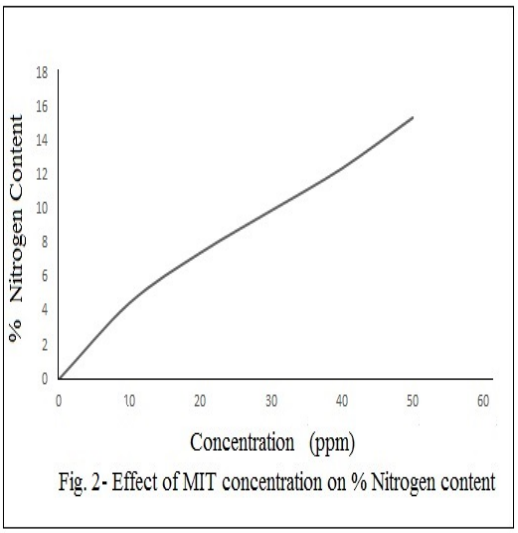


Fig. 2- Effect of MIT concentration on % Nitrogen content

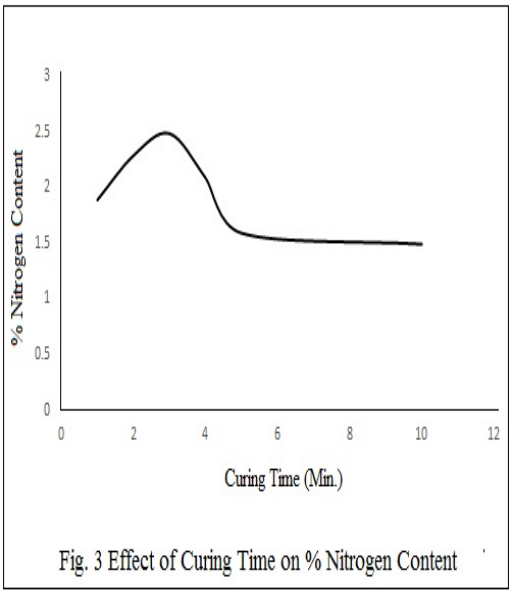


Fig. 3 Effect of Curing Time on % Nitrogen Content

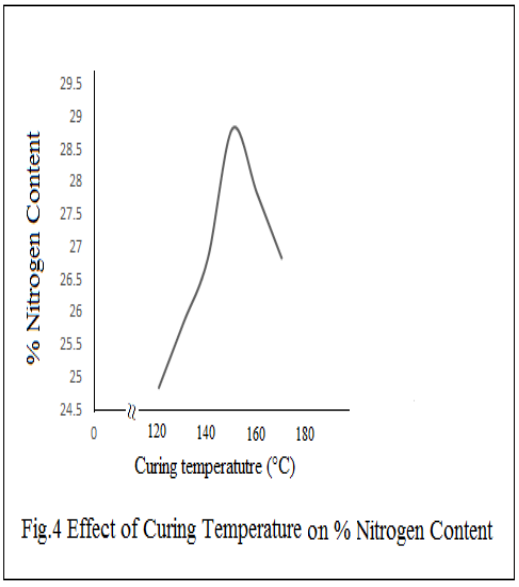


Fig.4 Effect of Curing Temperature on % Nitrogen Content

decomposition for MIT would take place.

Effect of Curing Temperature

From Fig. 4, it is indicated that by using padding technique where the MIT concentration is 50 ppm, curing time 1min. and using different curing temperature (120-170 °C). It was found that N% content increases up to 150°C and then it deceases again. This may be attributed to the fact that beyond 150°C a partial thermal decomposition for MIT would take place leading to lower n content.

Effect of Treatment on Morphological Structure

Figure 5 (a-d) shows the SEM for the treated cotton fabric samples with MIT concentration of 50 ppm, by padding technique, the samples after treatment, dried at 100° C and then cured at(120-150°) for 3 min. The involvement of MIT into the amorphous structure of the cotton fabric was appeared indicating the optimal conditions where sample cured at 150° shows better N-content and more deposition of MIT into cotton lattice. [11]

FT-IR Spectroscopic measurement

As shown in Fig. 6 the FT-IR spectra of Cotton/MIT composite, in the spectrum of MIT after using padding technique using 50 ppm MIT, cuing temperature 150° C and 3 min. the

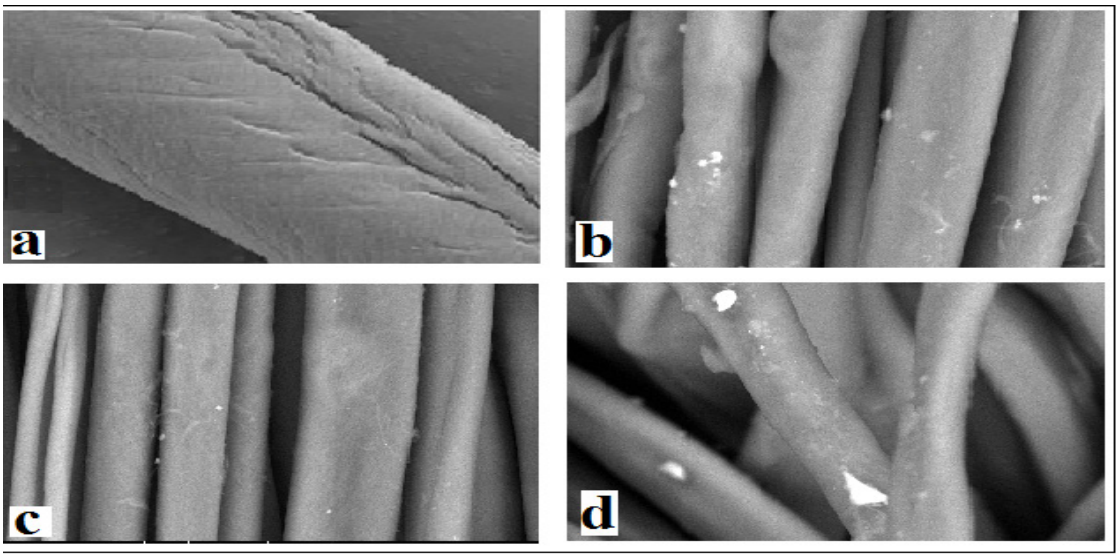


Fig. 5. Effect of Treatment on Morphological Structure a- Scoured cotton, b- Cotton/MIT cured at 120°C, c-Cotton/MIT cured at 130°C and d-Cotton/MIT cured at 150°C (magnification 6000 Time).

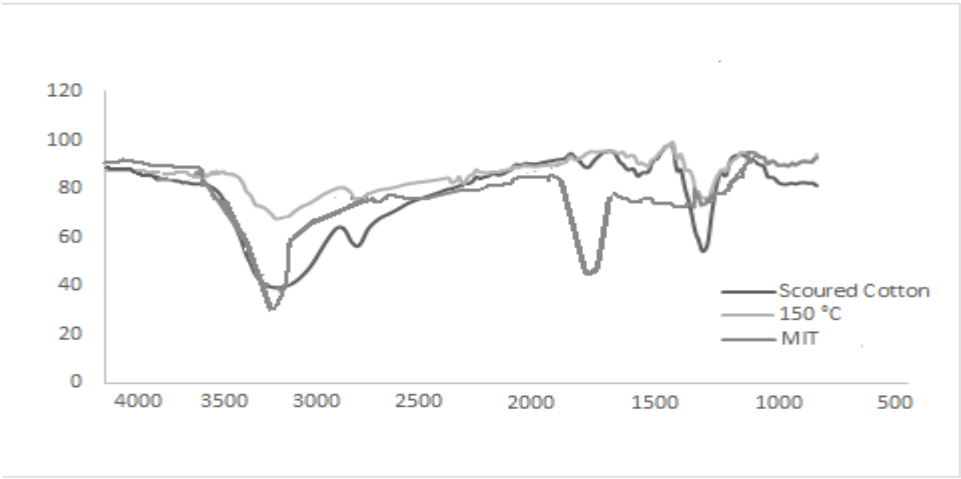


Fig. 6. FT-IR graph for Scoured cotton fabric, Methylisothiazolinone and treated cotton Sample cured at 150° C for 3 min.

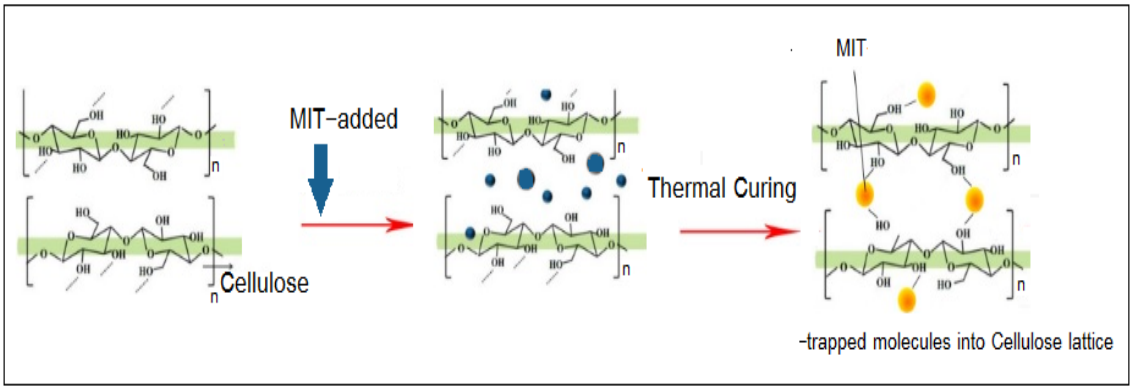


Fig.7 Mechanism of MIT-trapping into cellulose

characteristic peak appears at 1654 Cm^{-1} (C=O str.), 714 Cm^{-1} (C-S Str.) and 1413 Cm^{-1} (-CH_3 bend.) the FT-IR spectra for Cotton/MIT were at band 1650 Cm^{-1}, Furthermore, the intensity of the absorbent band of -C-OH str. (1029 Cm^{-1}) on cellulose chain became weaker and shifted to 1021Cm^{-1} suggesting that some changes occurred at the hydroxyl group of cotton. These results indicated that MIT was bound to cotton chain and was entrapped inside cotton lattice and this effect is clear at 150° C cured sample as shown by Fig. 7 [12 and 13].

Effect of Treatment on Antibacterial Behavior

TABLE 1. Anti-bacterial activity of different treated and cured samples at different temperature at fixed time (3 Min.).

Sample	Anti-bacterial activity %	
	Gram positive (S. Aureus)	Gram negative (E. Coli)
Blank Sample (Scoured cotton)	0	0
Sample Cured at 120°C for 3-min.	30	40
Sample Cured at 130°C for 3-min.	63	70
Sample Cured at 150°C for 3-min.	92	98

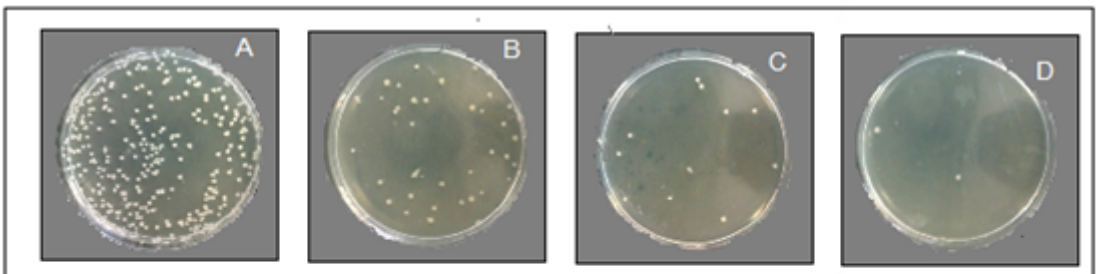


Fig.8 Anti-bacterial Activity of Cotton fabrics treated with MIT using different curing temperatures for 3 min. a- Blank sample , b-at 120°C , c-at 130°C and d- at 150°C using gram positive bacteria *S.Aureus* bacteria

According to AATCC antibacterial determination indicated in Table 1 and Fig. 8 it was clear that using the Padding technique using 50ppm of MIT then drying at 100°C for 2 min. followed by curing at Temperature 150° C for 3 min. gave the best results for inhibiting the growth of both gram positive and Gram negative bacteria. The result of antibacterial activity in gram negative bacteria is more than that of Gram positive one since Gram-positive bacteria have a thicker and more rigid peptidoglycan cell wall [14].

Conclusion

Using MIT as a preservative substance in new application for acquiring the antibacterial activity for treated Cotton fabrics. Where the work concentrated on using padding and exhaustion techniques using the same concentration of MIT and finding that padding techniques gave better nitrogen content more that of the exhaustion technique. So, the research dealt with using different concentrations of MIT and by varying the Treatment conditions such as curing time (1-5 min.) and curing temperature (120-170C). Comparing the treated fabrics with untreated ones assured that using treatment including 50 ppm of MIT at a curing temperature 150°C for 3 minutes gave a higher anti-bacterial performance which was emphasized by SEM, FT-IR spectrometry and by anti-bacterial tests against gram positive and gram negative bacteria.

References

1. Jerschow E., Hostynek J.J., Maibach H.I., Allergic contact dermatitis elicitation thresholds of potent allergens in humans**,** *Food Chem. Toxicol.* **39**, 11, 1095-1108 (2001).

2. Hyang Y. K., Yong J. L., Kyu-Bong K., Analytical method development of Methylisothiazolinone, a Preservative, in rat plasma using LC-MS/MS, *Journal of Chromatography B,* 1100– 1101, 27–323 (2018).

3. Erol C., Tuna O., Sevki K., Ilhan A., Antimicrobial agents, triclosan, Chloroxylenol, Methylisothiazolinone and borax, used in cleaning had genotoxic and histopathology effects on rainbow trout, *Chemosphere,* **182**, 720-729 (2017).

4. Urwin R., Wilkinson M., Methylchloro isothiazolinone and Methylisothiazolinone contact allergy: a new Epidemic'. *Contact Dermat.* **68**, 253–5 (2013).

5. Kandavelu V., Kastien H., Thampim K. R., Photocatalytic degradation of isothiazolin-3-ones in water And emulsion paints containing noncrystalline TiO_2 and ZnO catalysts, *Applied Catalysis B: Environmental,* **48**, 101-111 (2004)

6. Mori H. H., Yamaguchi Y., Shibata Y., Senda K., Yamaguchi T. M., Senda S., Monitoring of Anti-fouling booster biocides in water and sediment from the port of Osaka, *Japan, Arch Environ. Contam. Toxicol*, **48** (3), 303–310 (2005).

7. Schwensen JF., Lundov MD, Bossi R., Banerjee P., Gimenez-Arnau E., Lepoittevin JP., Liden C., Uter W., Yazar K., White IR., Johansen JD., Methylisothiazolinone and Benzisothiazolinone are widely used In paint a multicenter study of paints from five European countries. *Contac*t *Dermat,* **72**, 127–38 (2015).

8. Hou QX, Liu W., Liu ZH., Duan B., Bai LL., Characteristics of antimicrobial fibers prepared with wood Periodate oxycellulose, *Carbohydr Polym,* **74**, 235–240 (2008).

9. American Association of Textile Chemistry & Colorists, Antibacterial activity Assessment of Textile Material, (AATCC), 147, USA. (2004).

10. El-Alfy E. A., Attya M. and Shaaban M. F., Treatment of cotton fabrics to inhibit Bacterial effect of some Micro-organisms part I-using separate nano antibacterial agents, *Egypt. J. Chem.,* **6**, 671-680 (2015).

11. Hofmann M. A., Gimenez-Arnau A., Aberer W., Bindslev-Jensen C., Zuberbier T., MI (2-methyl-4-isothia zolin-3-one) contained in detergents is not detectable in machine washed textiles Hofmann et al. Clin. *Transl Allergy*, **8**, 1 (2018).

12. Liu K., Lin X., Chen L., Huang L., Cao S., Dual-functional chitosan–Methylisothiazolinone/microfibri-llated cellulose biocomposites for enhancing antibacterial and mechanical properties of agar films, *Cellulose*, **21**, 519–528 (2014).

13. Bitao F., Shujun C., Qiufang Y., Qingfeng S., Chunde J., Fabrication of Cellulose Nanofiber/AlOOH Aerogel for Flame Retardant and Thermal Insulation, *Materials,* **10**(3), 311 (2017).

14. Das D., Ara T., Dutta S., Mukherjee, A new water resistant biomaterial biocide film based on guar Gum, *Bioresource Technol.,* **102**, 5878–5883 (2011).

تحسين قدرة الأقمشة القطنية علي مقاومة البكتيريا عن طريق استخدام مادة الميثيل ايزوسيازولينون

محمد فكري شعبان و أحمد سعد منتصر
شعبة بحوث الصناعات النسجية - المركز القومي للبحوث - الجيزة - مصر.

أن مادة الميثيل ايزوسيازولينون لها استخدامات عديدة كمادة حافظة في صناعات عدة مثل صناعة البويات وايضا في مياه أبراج التبريد بمحطات توليد الطاقة كما أن لها استخدامات واسعة في مستحضرات العناية بالجسم والجلد والدراسة الحالية هي محاولة لإعادة توظيفها في مجال جديد عليها وهو معالجة الأقمشة القطنية بهدف زيادة قدرتها علي منع النمو البكتيري في الملابس القطنية المعالجة بتلك المادة.

وفي سبيل ذلك تم استخدام طريقة ال Cold pad-dry-Thermofixation لعينات مختلفة بتركيزات مختلفة (١٠ : ٥٠ جزء/مليون) وعند درجات تحميص من (١٢٠ : ١٧٠ درجة مئوية) عند أزمنة مختلفة (١:٥ دقائق) ولقد تم استخدام العديد من التقنيات المختلفة لدراسة سلوك المنتج مثل التصوير الاليكتروني الميكروسكوبي- الأشعة الفوق بنفسجية قياس القدرة علي القضاء علي البكتيريا سالبة وموجبة الجرام واتضح من تلك النتائج أن المعالجة بتركيز ٥٠ جزء/مليون عند درجة تحميص ١٥٠ درجة لمدة ٣ دقئق اعطت افضل النتائج وقضت علي نحو ٩٨٪ من البكتيريا سالبة الجرام ونحو ٩٦٪ من البكتيريا موجبة الجرام مما يشكل نجاحا في استخدام مادة الميثيل ايزوسيازولينون في القضاء علي البكتيريا والكائنات الدقيقة بالمنسوجات القطنية