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Preparation of durable insect repellent cotton fabric: Limonene as insecticide

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ABSTRACT

Limonene, an important insecticide, was applied to cotton fabrics as per the conventional impregnation and coating methods in addition to an innovative technology based on prior modification of the fabric via grafting with monochlorotriazinyl-β-cyclodextrin (MCT-β-CD). Emulsion of limonene and polymeric binder were used when the conventional methods were employed to place limonene in the fabric while inclusion of limonene fragrance in the cavities of β-cyclodextrin molecules constitutes the means of limonene fixation onto the fabric in the innovative technology. Bioassay test results expressed as repellency, knockdown and mortality were taken as a measure of toxic activity. The effect of washing and storing on the biocidal activity of fabrics treated according to the three aforementioned technologies was studied.

1. Introduction

Worldwide, mosquitoes transmit disease to more than 700 million people annually and are responsible for the deaths of 1 of every 17 people currently alive (Fradin, 1988). Malaria results from infection with a protozoan carried by mosquitoes and according to reports from the World Health Organization (WHO), causes as many as 3 million deaths annually.

Thus one of the approaches for control of these mosquito-borne diseases is the interruption of disease by killing or preventing mosquitoes to bite human beings. Insecticide-treated bed nets were practicized to reduce all child mortality significantly in Africa due to effective personal protection against malaria vector *Anopheles* mosquitoes. Insecticide-treated bed nets are now being promoted strongly as a malaria control tool in Africa by the World Health Organization and other international agencies (Heal, Surgeoner, & Liday, 1995; Hewitt, Rowland, Muhammad, Kamel, & Keup, 1995; Lillie, Shreck, & Rah, 1988; Michael, Uedelhoven, & Robbins, 2003).

Cyclodextrins are produced by enzymatic degradation of starch. Cyclodextrins are cyclic oligosaccharides. Monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) is the first reactive cyclodextrin derivative manufactured on an industrial scale (Voncina & Majcenle Marechal, 2003). B-cyclodextrin (β-CD) is commercially most interesting because of its simple production, availability, cavity diameter and price. The inner diameter of the β-CD cavity can accommodate aromatic compounds such as volatile molecules and drugs (Szejtle, 1998; Szejtle, 1982).

The new concept for the modification of textile substrates is based on permanent fixation of supramolecular compounds such as CDs, on the material surface, which impart new functionality to the fabric (Knittel & Schollmeyer, 2000). Textile substrates treated in this way will be important for medical, hygienic textiles, garment and home textiles.

Previous study was carried out on the inclusion ability of MCT-β-CD finished cotton fabrics towards insect repellent. The results show that increasing the amount of MCT-β-CD fixed on textiles corresponding to increased amount of complexed molecules. (Abdel-Mohdy, Rehan, Ragaei, & Aly, 2007).

Limonene occurs naturally in citrus and other fruits, vegetables, meats and spices. Limonene is used in many food products, soaps and perfumes for its limon-like flavor and odor. Limonene also is a registered active ingredient in 15 pesticide products used as insecticides, insect repellent, dog and cat repellents. Limonene was first registered as an insecticide in the U.S. in 1985. It was registered as an antimicrobial in 1971, and as a dog and cat repellent in 1983 (Prevention, Pesticides & Toxic Substances, 1994).

This work is undertaken with a view to produce cotton fabrics having the functionality of durable limonene-based insecticide. The conventional impregnation methods as well as the surface coating method are employed for fabric treatments. An innovative method based on forming inclusion complexes with MCT-β-CD

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treated fabrics using limonene as guest molecules is also described.

2. Experimental

2.1. Materials

Mill scoured, bleached and mercerized plain weave cotton fabric (169 g/m^2), kindly supplied by "Misr Company for Spinning and Weaving; Mehalla El – Kobra, Egypt" was used. The fabric was further laboratory purified by scouring at 100 °C for 60 min in a solution containing 2 g/L sodium carbonate and 5 g/L Egyptol. It was then thoroughly washed with water and left to dry in air at room temperature.

Monochlorotriazinyl-β-cyclodextrin was provided by Wacker-Chemie Gmbh, Munchen, Germany.

2.2. Fixation of MCT-β-CD onto cotton

The conventional pad-thermo fixation method was applied (Abdel-Mohdy, El-Aref, Hashem, & Aly, 2005). Thus, cotton samples were impregnated in alkaline solution containing MCT-β-CD and squeezed to 100% wet pick-up. After drying the samples were subjected to thermo fixation followed by washing with water and finally dried under the normal laboratory conditions.

The grafting yield of MCT-β-CD in the treated cotton fabrics was evaluated in terms of nitrogen content values estimated as per the Standard Kjeldahl method (Vogel, 1975). Grafted-β-CD molecules on the textile substrate were determined with phenolphthalein method (Geoel & Neme, 1995).

2.3. Insect repellent treatment

2.3.1. Untreated sample

Cotton fabrics were soaked in water that did not contain any insecticide, and then left in ambient conditions for 4 h to dry.

2.3.2. Control sample

Cotton fabrics were soaked in a solution containing the insecticide in ethanol for 5 min and squeezed to 100% wet pick-up, and then air dried for 4 h. After complete drying, samples were packed in poly ethylene bags.

2.3.3. Treated samples

- Impregnation method: cotton fabrics were soaked in a solution containing different doses of limonene, polyvinyl acetate emulsion as a binder and arkofix as a crosslinking agent.
- Surface coating method: the coating on one surface of the fabric could be effected by using a solution containing a dispersion of an insecticide (limonene) and polyvinyl acetate in the form of viscous liquid. This dispersion could be applied directly to the fabric and spreaded in a uniform manner.
- Samples of MCT-β-CD treated cotton were padded with an ethanolic solution of insecticide to wet pick-up of 100%, and then left in air to dry for 4 h.

2.4. Washing procedure

Cotton fabrics were washed once in an aqueous solution containing 2 g/L sodium carbonate and 5 g/L liquid soap (Egyptol), at 60 °C for 15 min.

2.5. Laboratory bioassay test

The bioassay test results are expressed as repellency, knockdown and mortality. The bioassay tests of the treated fabrics were measured using Standard World Health Organization (WHO) tests (Ansari, Kapoor, & Sharma, 1998; Kapoor & Anari, 2003; World health Organization, 1998). These tests were conducted in parallel with a blank and untreated (control) samples.

Repellency, knockdown and mortality rates observed after different time intervals were corrected using the Abbott's formula (Abott, 1925).

$$\%\text{correctedaction} = \frac{\%\text{Observedaction} - \%\text{untreatedaction}}{100 - \%\text{untreatedaction}} \times 100$$

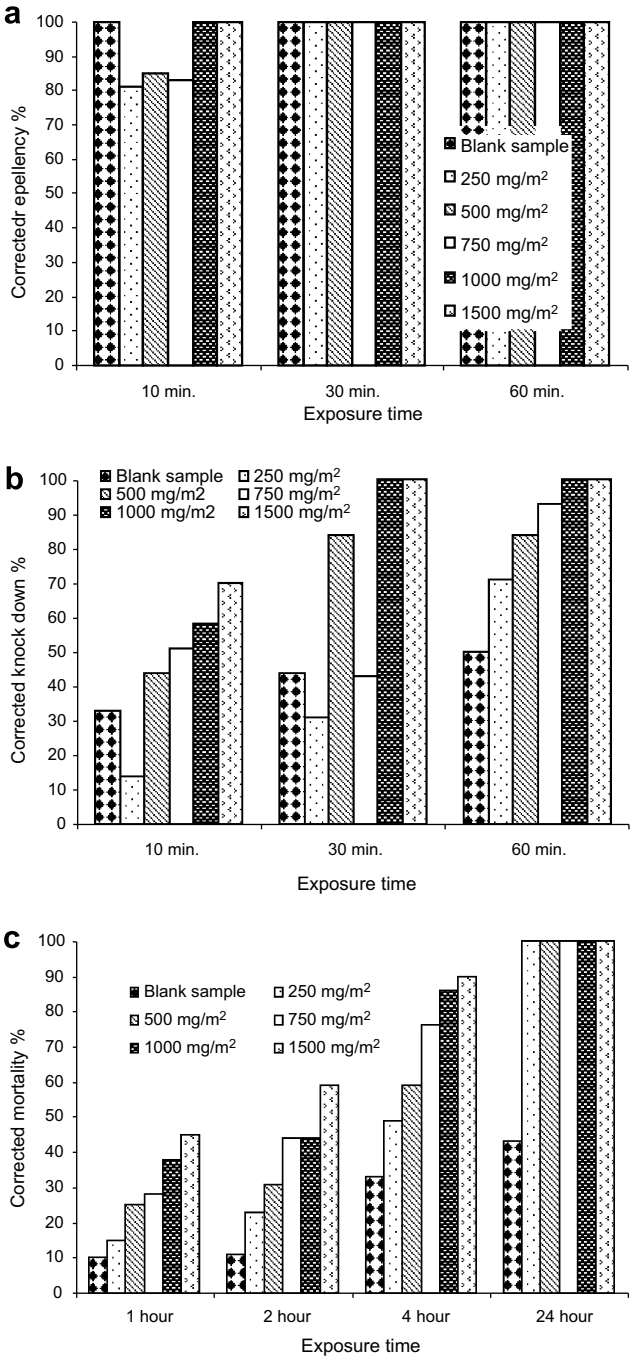

Fig. 1. Relation between insecticide doses-treated fabrics and toxic activity. Treatment condition: Impregnation method. [limonene], 250–1500 mg/m^2; [arkofix], 1.7 g/m^2; [PVAc.], 3.4 g/m^2; pick-up, 100%. Blank sample: cotton fabric treated with limonene only (1000 mg/m^2).

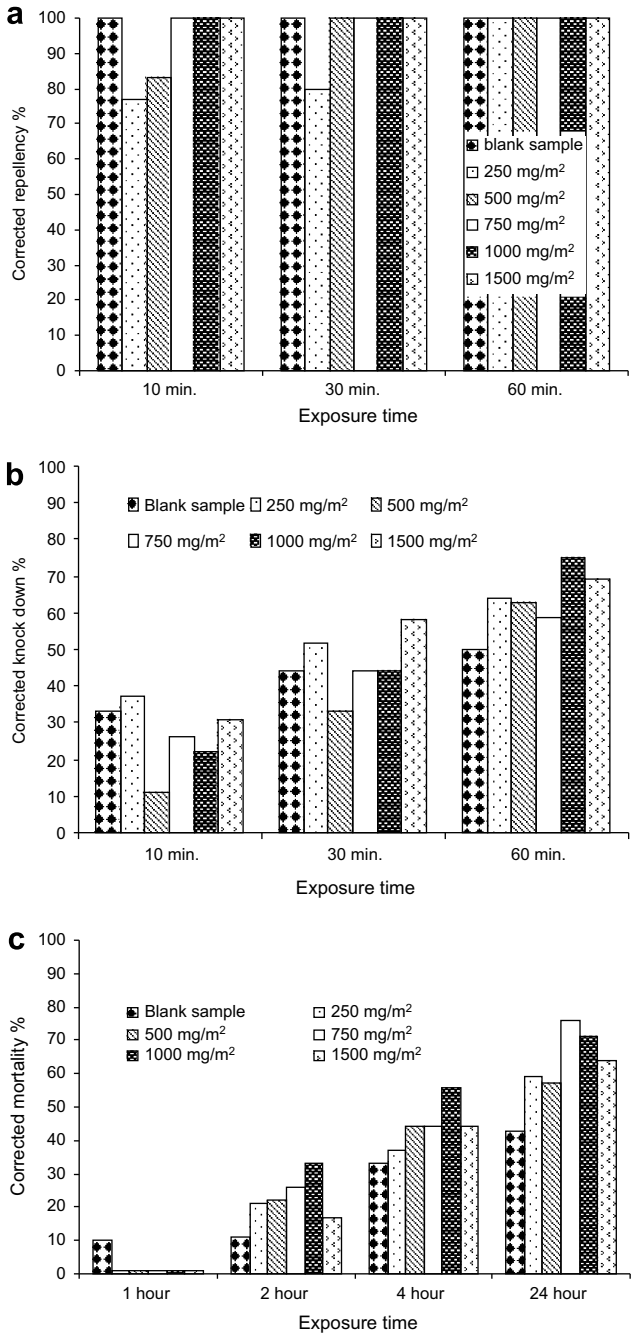

Fig. 2. Relation between insecticide doses-treated fabrics and toxic activity. Treatment condition: surface coating method [Limonene], 250–1500 mg/m^2; [arkofix], 3.4 g/m^2; [PVAc.], 20%; pick up, 100%. Bioassay: for coated surface. Blank sample: cotton fabric treated with limonene only (1000 mg/m^2).

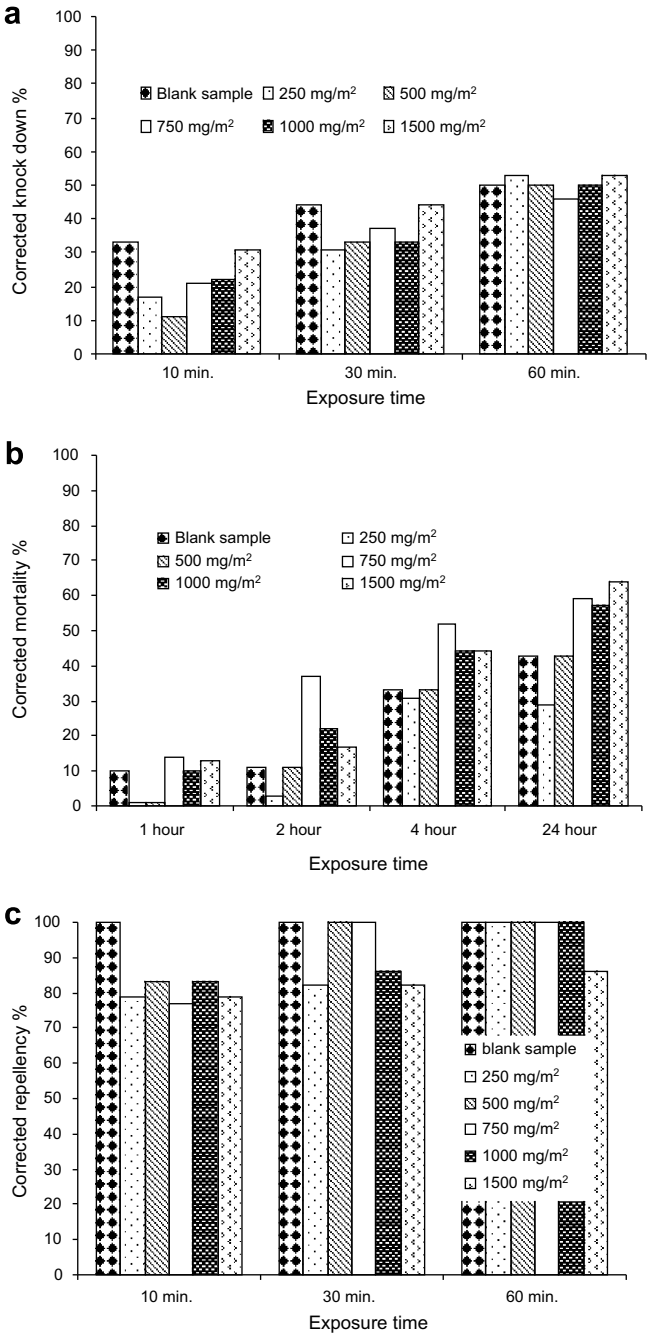

Fig. 3. Relation between insecticide doses-treated fabrics and toxic activity. Treatment condition: surface coating method [Limonene], 250–1500 mg/m ^{2}; [arkofix], 3.4 g/m^2; [PVAc.], 20%; pick-up, 100%. Bioassay: for the back of the coated surface. Blank sample: cotton fabric treated with limonene only (1000 mg/m^2).

2.6. Scanning Electron Microscopy (SEM)

SEM analysis of treated fabrics was performed using a JEOL (JXA – 840 A); Electron Probe Micro-Analyzer, Edward [England], 150 A. Sputter Coater; at Scanning Electron Microscope Division; Central Services Laboratory, National Research Centre. Samples were coated with gold according to the method described in the operation manual provided by the manufacturer.

3. Results and discussion

3.1. Bioassay test results

3.1.1. Impregnation method

The toxic activity against mosquitoes is expressed as repellency, knockdown and mortality actions. Fig. 1 shows bioassay test results expressed as corrected repellency knock down and mortality obtained with treated cotton fabrics, and blank samples. Bioassay

test results show that the repellency, knockdown and mortality values of the fabric treated by the impregnation method are nearly equal to those of the blank samples. It is also observed that the impregnated fabrics display lower initial knockdown activity against mosquitoes. This is in accordance with previous studies (Abdel-Mohdy, Fouda Moustafa, Rehan, & Aly, 2008) which ascribed this to diffusion of the polymer containing insecticide inside the fabric structure and in so doing, reduces the amount of insecticide available on the fiber's surface thereby reducing biocidal activity.

It is also seen (Fig. 1) that the slower knockdown and instant killing action of insecticide-treated fabrics are observed in the being of exposure. This suggests that part of the mosquitoes would land directly on the fabric surface to be knockdown and becomes exposed to high absorption of insecticide enough for quick killing action.

3.1.2. Surface coating method

The cotton fabrics were coated on one side (one surface) by polymer containing different doses of the limonene insecticide. Bioassay test was performed through evaluating the toxic activity

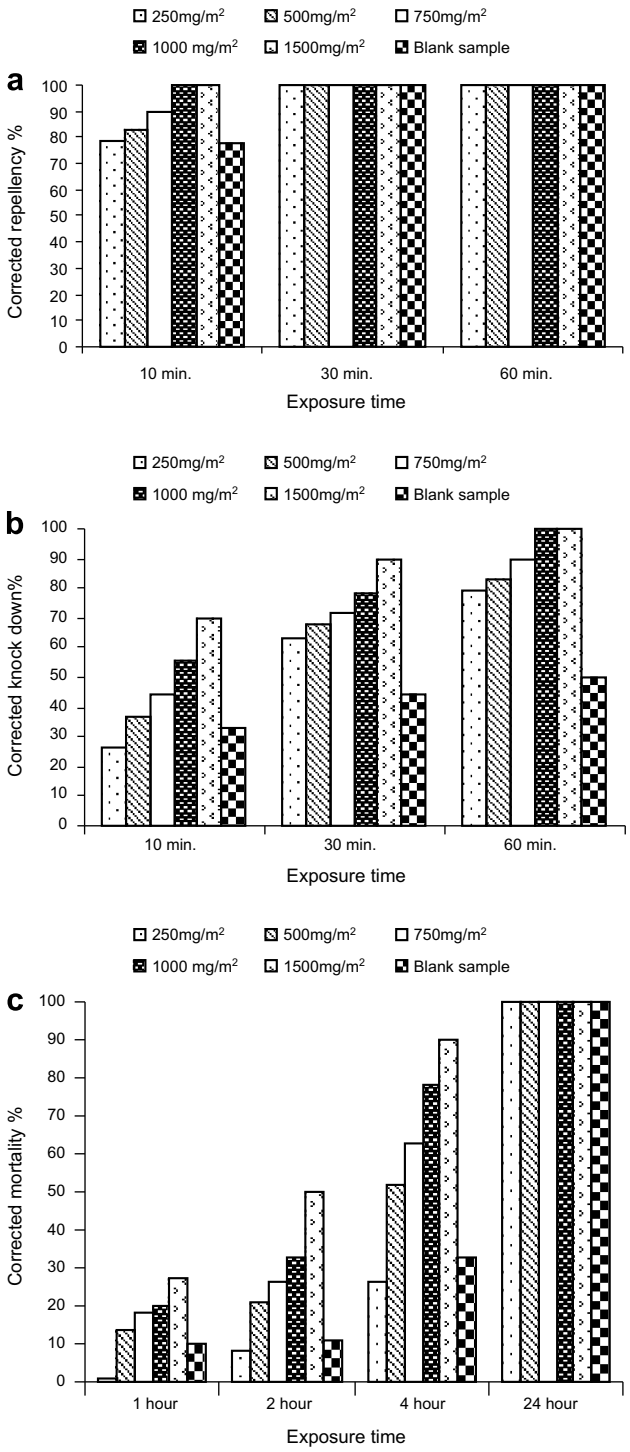

Fig. 4. Relation between insecticide doses-treated fabrics and toxic activity. Treatment condition: inclusion complexes of fixed MCT-β-CD with insecticide [limonene], 250–1500 mg/m^2; [MCT-β-CD- finished cotton fabric], 19%; Pick-up, 100%. Blank sample: cotton fabric treated with limonene only (1000 mg/m^2).

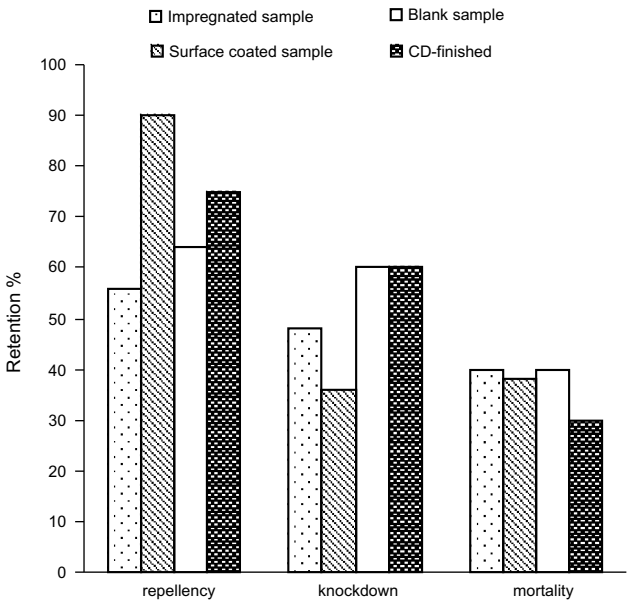

Fig. 5. Effect of washing on the retention of corrected toxicity % of Insecticide-treated fabrics.

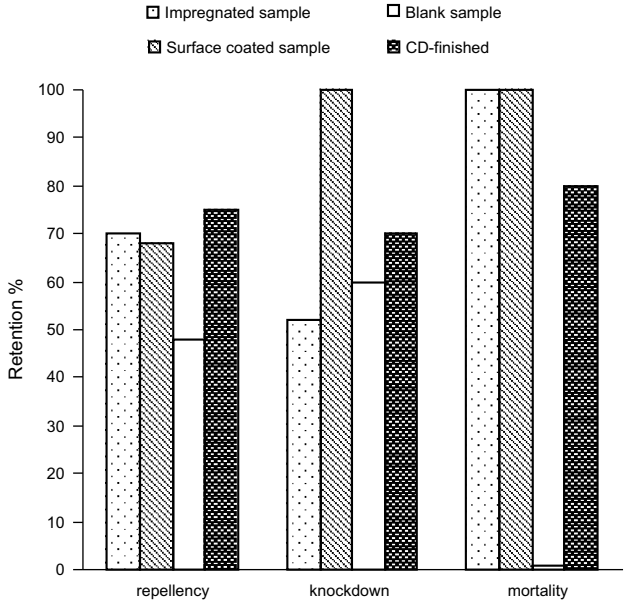

Fig. 6. Effect of ageing on the retention of corrected toxicity % of insecticide-treated fabrics.

against mosquitoes of the limonene-treated fabric surface, and the back surface as well.

Results of Fig. 2 show the toxic activity of the coated surface. The results imply that the surface coating method provides high personal protection against mosquitoes especially the repellent action (about 100%). The results (Fig. 2) indicate that the knockdown activity and the mortality action of coated fabric surface are slightly higher than those of the blank samples, especially at the higher concentrations of limonene.

Fig. 3 shows the toxic effect of the back of the coated surface against mosquitoes. It is clear that the back of the coated fabric surface is toxically effective against mosquitoes. Mosquito repellency rates are high and fast especially on using high concentrations of the insecticide in the coating polymer. Results of Fig. 3 signify that the knockdown effect of the back of the coated fabric surface is nearly the same as the blank sample. For the mortality action, the back of the coated fabric surface is more effective than those of the blank sample.

A comparison between the results of Fig. 3 and the corresponding results of Fig. 2 would signify that the toxic activity for the back of the coated fabric surface is lower than that of the coated surface.

3.1.3. Inclusion complexes of fixed MCT-β-CD with insecticide

Limonene bioassay results of tests undertaken after treatment of the fabrics are shown in Fig. 4. Bioassay results show the toxic activity of MCT-β-CD finished cotton fabrics treated with different doses of limonene, and also show the effect of exposure time against mosquitoes. The results show that the repellent, knockdown and killing action against mosquitoes increased with increasing concentration of limonene in MCT-β-CD finished cotton fabrics within the range studied (250–1500 mg/m^2). Also, results show that the corrected activity (repellency, knockdown and mortality) increased by increasing the exposure time.

The results indicate, the repellency, knockdown and mortality values of MCT-β-CD finished cotton fabrics treated with limonene are higher than those of the blank sample.

By and large, the toxic activity against mosquitoes of the limonene-treated as per all the methods used, increases by increasing the concentration of insecticide on the fabric as well as by prolonging the exposure time (Figs. 1–3).The toxic activity of all limonene-treated cotton fabrics (irrespective of the treatment method used) shows that fast repellency, slower knockdown and instant killing actions were observed at the beginning of exposure. These results are in conformation with those encountered with the impregnation method as part of mosquitoes under investigation that land directly on the treated fabric surface will often knockdown and be exposed to high absorption of insecticide enough for quick killing action.

3.2. Effect of washing on limonene-treated fabrics

Fig. 5 shows the effect of washing on the retention percent of toxic activity of treated fabrics. Obviously, insecticide-treated fabrics prepared using impregnation and surface coating methods as well as blank sample display insecticidal activity after washing. The results in (Fig. 5) show that insecticidal activity after washing of the treated fabrics is high when compared with the blank sample.

3.3. Effect of ageing on limonene-treated fabrics

Limonene bioassay test results expressed as repellency, knockdown and mortality of treated fabrics and blank samples after 18 months storage are shown in Fig. 6. It is clear that the toxic activity for all treated and blank fabric samples decreases by time. However fabrics treated according to the three mentioned methods produce high percent of mortality in mosquitoes beside high repellency and knockdown effect, even after about 18 months. As expected, the values of retention percent of treated samples after storage are significantly higher than those of the blank sample.

3.4. Scanning Electron Microscopy

Fig. 7 depicts the scanning electron microscope pictures for cotton fabrics treated with the polymer coating methods, as well as for untreated fabrics (control sample). The overall picture of control sample shows that the width of the fibers is completely uniform, the surface of the fibers are very smooth and homogeneous and very clear (Fig. 7a). The surface morphology of treated fabrics appear smooth, polymer layered and polymer trapped inside the fiber structure appear as small spots in impregnation method (Fig. 7b), and coated with polymer in surface coated method

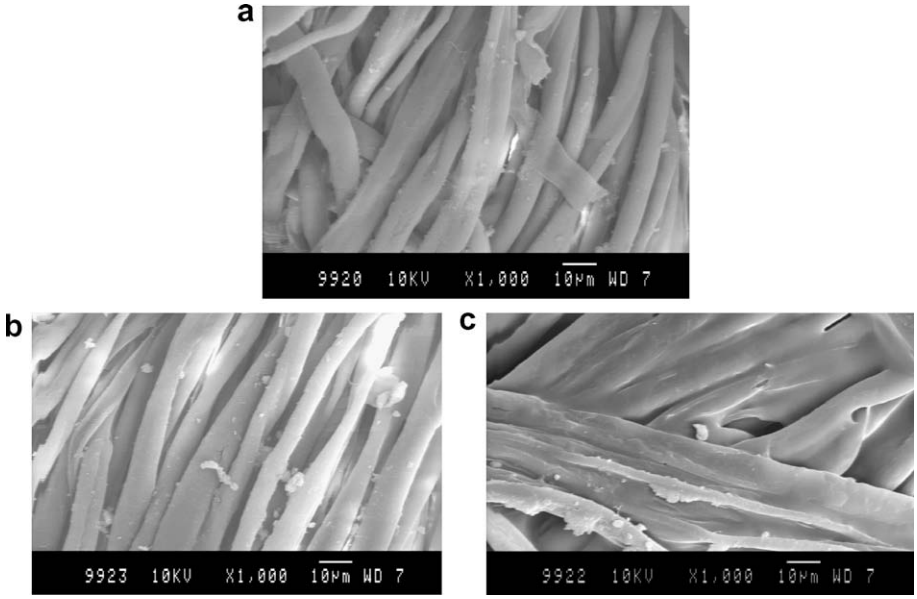

Fig. 7. (a) Untreated sample (b) impregnated sample (c) surface coated sample Scanning electron microscopy results of treated fabrics.

(Fig. 7c). This is rather similar to scanning electron microscope pictures obtained with permethrin insecticide when used for treatment of cotton fabrics using the impregnation method and the coating method (Denter, Buschmann, Knittel, & Schollmeyer, 1997; Knittel, Buschmdun, & Schollmeyer, 1991).

4. Conclusion

Treatment of cotton fabrics with a finishing formulation based on limonene using polymer coating methods and MCT-β-CD finished fabric method, imparts toxic activity against mosquitoes. The treated fabric can be washed and stored while keeping their insecticidal property.

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