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Repellency of controlled-release treated cotton fabrics based on cypermethrin and prallethrin

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Abstract

Monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) was fixed permanently onto the surface of cotton fabrics. The fixed MCT-β-CD forms inclusion complexes with insecticides (cypermethrin and prallethrin). MCT-β-CD-finished cotton fabrics loaded with insecticides are effective in reducing malaria morbidity and mortality due to effective personal protection against mosquitoes. Bioassays show that the treated fabrics have fast action against mosquitoes at the range of concentrations studied. The toxic activity of the treated fabrics increased by increasing the insecticide concentration in the treated fabrics, and also increased by increasing the exposure times. The quantitative analysis results show that there are great losses in the amount of insecticides in blank samples by washing, while treated fabrics retain high amount of insecticides.

Keywords: Insecticide; Insect repellent; Cypermethrin; Prallethrin; Cyclodextrin; MCT-β-CD

1. Introduction

Cyclodextrins are produced by the action of the enzyme cyclodextrin glucosyltransferase on starch. The most common cyclodextrins are α, β, and γ cyclodextrins having six (α), seven (β) or eight (γ) anhydroglucose unites in the ring structure. Cyclodextrins molecules can form inclusion complexes with a large number of organic molecules. The properties of cyclodextrins enable them to be used in a variety of different textile applications (Buschmann, Knittel, & Schollmeyer, 1990; Buschmann, Knittel, & Schollmeyer, 1991; Knittle, Buschmann, & Schollmeyer, 1991; Szejtli, 1982).

Monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) is the first reactive cyclodextrin derivative manufactured on an industrial scale (Bender, 1986). MCT-β-CD can be fixed on to cotton cellulose following a reactive dye reaction mechanism (Denter & Schollmeyer, 1996). Once chemically grafted onto cellulosic substances, these materials can be used for fragrance release, odor adsorption, controlled release, ultraviolet protection and stabilization of active ingredients (Lo Nastro, Eratani, Ridi, & Bagliani, 2003).

Among the increasing number of arthropod-borne diseases, only few are preventable by vaccines. For this reasons, personal protective measures against bitting arthropods and arthropod-borne diseases constitute the first line of defense.

A major advance in the protection of high risk personnel (e.g. outdoor workers, soldiers and travelers) has been the development of topical repellent formulations and residual insecticides that can be impregnated into clothing, tents and netting (Faulde & Uedelhoven, 2006).

To date, six pyrethroid insecticides (α-cypermethrin, cyfluthrin, deltathrin, etofenprox, λ-cyhalothrin and permethrin) have been recommended by the World Health Organization (WHO) in the frame work of the World Health Organization Pesticide Evaluation Scheme (WHOPES) for the treatment of mosquito nets (Haugaard, Duchan, Zaim, & Guillet, 2002).

Previous study was carried out on the inclusion ability of MCT-β-CD-finished cotton fabrics towards insect repellents (Abdel-Mohdey, Rehan, Ragaei, & Aly, 2007). The

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results show that increasing the amount of MCT-β-CD on textiles corresponding to increased amount of complexes molecules. The inclusion of insect repellents could be achieved and kept during storage for more than 12 months as a test period, and released again in controlled manner.

In our research, we fixed MCT-β-CD onto cotton fabrics via treated by soaking in insecticide solution (cypermethrin and prallethrin). The aim of this study is to obtain a wash durable insecticide treated fabrics wherein the active ingredient is easily incorporated into the fabric and is prevented from being washed off, thereby maintaining the insecticide at the fabric surface to permit interaction with target arthropods for a prolonged period of time, even after repeated washing.

2. Experimental

2.1. Materials

Mill scoured, bleached and mercerized plain weave (169 g/m^2) cotton fabric, supplied by Misr Company for Spinning and Weaving, Mehalla – El – Kobra, Egypt was employed. The fabric was further laboratory purified by scouring at 100 °C for 60 min in a solution containing sodium carbonate (2 g/l). It was then thoroughly washed with water and dried at ambient temperature.

Monochlorotriazinyl-β-cyclodextrin was provided by Wacker – Chemie GmbH, Munchen, Germany. Other chemicals used, were reagent grade and obtained from commercial sources.

The insecticides used, cypermethrin and prallethrin were kindly supplied by El-Nasr Co. Intermediate Chem., Cairo, Egypt.

Cypermethrin is an odorless crystal (pure), a yellow-brown viscous semi-solid at ambient temperatures. The structure of cypermethrin was established on the basis of its spectral data studies. The IR spectrum showed bands at: 3428 cm^{-1} (N—H) 3080 cm^{-1} (C—H vinylic); 2738 cm^{-1} (C—H alkane, CH_3), 2260 cm^{-1} (C≡N), 1761 cm^{-1} (C=O ester); 1654 cm^{-1} (C≡C), 1585 cm^{-1} (C=C aromatic); 1488 cm^{-1} (O—C=O symmetric stretching); 1382 cm^{-1} (C—O ether), 1151 cm^{-1} (C—O—C antisymmetric) and 857 cm^{-1} (C—Cl).

Prallethrin is a yellow to yellow-brown liquid. The structure of prallethrin was established on the basis of its spectral data studies. The IR spectrum showed bands at: 3291 cm^{-1} (≡C—C—H alkyne); 2925 cm^{-1} (C—H alkane); 2122 cm^{-1} (C≡C); 1716 cm^{-1} (C=O ester); 1660 cm^{-1} (C=O ring); 1420 cm^{-1} (O—C=O symmetric stretching), 1383 cm^{-1} (C—O ether); and 1154 cm^{-1} (C—O—C antisymmetric).

2.2. Grafting of cotton fabrics with MCT-β-CD

The permanent grafting of MCT-β-CD was carried out by the dipping of cotton samples (25 × 25) for 5 min at room temperature in aqueous solution of MCT-β-CD and sodium carbonate (20 g/l) under magnetic stirring, and then they were carefully squeezed. To minimize the reaction of MCT-β-CD with air moisture, the impregnated sample was treated in an oven at 130 °C for 15 min (Abdel-Mohdey, El-Aref, Hashem, & Aly, 2005). The treated samples were then washed with water to remove non-reacted matter and finally dried under 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 a standard Kjeldahl method (Vogel, 1975).

2.3. Insect repellent treatment

2.3.1. Control sample (untreated sample)

Cotton fabrics were soaked in water that did not contain any insecticide, then air dried for 4 h.

2.3.2. Blank sample

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

2.3.3. Treated sample

A divided samples of MCT-β-CD treated cotton is applied in an ethanolic solution of insecticide, to wet pick – up of 100%, samples after padding are left to dry in air to complete loading of insecticide to the treated cotton fabric.

2.4. Washing procedure

Washing of the blank and treated fabrics was carried out gently with soap under controlled laboratory conditions. Cotton fabrics were washed in an aqueous solution containing 2 g/l sodium carbonate and 5 g/l liquid soap (Egyptol) at 60 °C for 15 min for one wash.

The effect of MCT-β-CD-finished fabrics on its ability to keep insecticide fragrance, after washing, is expressed in percent retention. Retention is the percentage of add-on left after the mild refinish wash:

$$\text{Retention } \% = \frac{\text{Activity after washing}}{\text{Activity before washing}} \times 100$$
$$= (\text{Amount of insecticide after}/\text{Amount of insecticide before}) \times 100$$

2.5. Laboratory bioassays

Repellent effect, knockdown effect and mortality resulting from tarsal contact with treated material were measured using standard World Healthy Organization (WHO) tests.

The number of repellent and knockdown mosquitoes were recorded at fixed intervals (every 10 min depending

on repellent and knockdown rates) for 60 min. The mosquito mortality was observed after 1–24 h.

These tests were conducted in parallel with a control sample with no insecticide (untreated).

Repellency, knockdown and mortality rates were corrected using Abott formula (Abott, 1925):

2.6. Determination of insecticide in treated fabrics

In the present study, a fast, selective and sensitive method of insecticide analysis in treated cotton fabric using gas chromatography (GC) with electron capture detection for quantification of the insecticides.

Analysis of acetone extracts was conducted with a Hewlett-Packar Model 5890 AGC, equipped with column HP-1 (25 m × 0.2 mm × 0.2 μm film thickness) and flam ionization detector (FID). The injector and detector were operated (at 250 and 280 °C), respectively. The oven temperature was programed from 200 to 250 °C at 5 °C/min and held for 1 min. The GC analysis was carried out at Mycotoxin center laboratory, National Research Center, Egypt.

3. Results and discussion

3.1. Bioassay test results

Chemical treatment of textiles, particularly those based on MCT-β-CD-finished cotton; to impart toxic effect against mosquitoes was carried out using two insecticides, cypermethrin which is recommended by World Health Organization (WHO) and prallethrin.

Insecticide bioassay results of tests undertaken after treatment of the fabrics are shown in Figs. 1–6. Bioassay results are represented as corrected toxic activity (corrected repellency, corrected knockdown and corrected mortality). For repellent and knockdown test, the number of mosquitoes are counted at different interval of time, viz., 10, 30

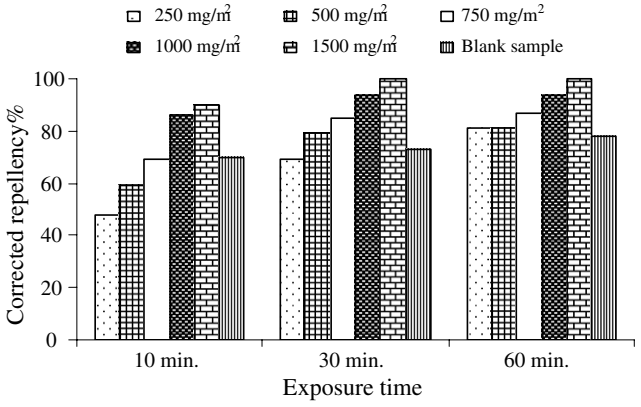

Fig. 1. Relation between cypermethrin doses-treated finished fabrics and corrected repellency % at different exposure times. MCT-β-CD-finished cotton fabrics 19%. Blank sample: cotton fabric treated with cypermethrin only (1000 mg/m^2).

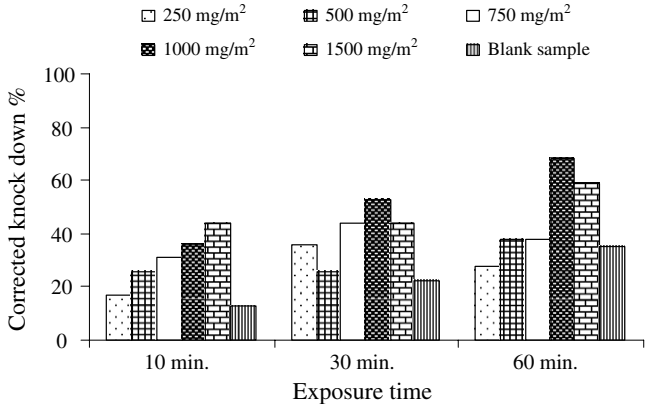

Fig. 2. Relation between cypermethrin doses-treated finished fabrics and corrected knockdown % at different exposure times. MCT-β-CD-finished cotton fabrics 19%. Blank sample: cotton fabric treated with cypermethrin only (1000 mg/m^2).

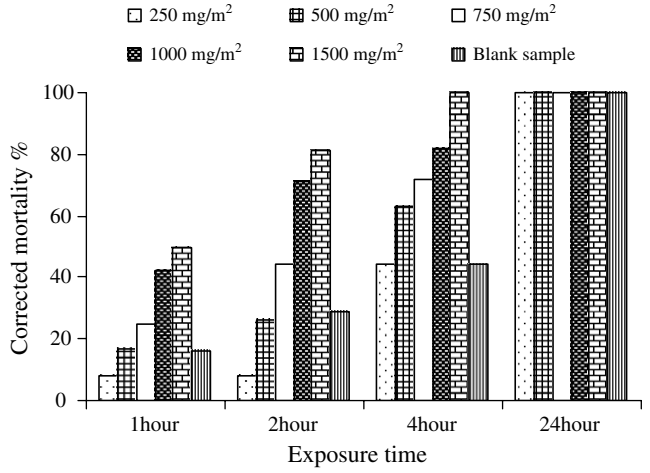

Fig. 3. Relation between cypermethrin doses-treated finished fabrics and corrected mortality % at different exposure times. MCT-β-CD-finished cotton fabrics 19%. Blank sample: cotton fabric treated with cypermethrin only (1000 mg/m^2).

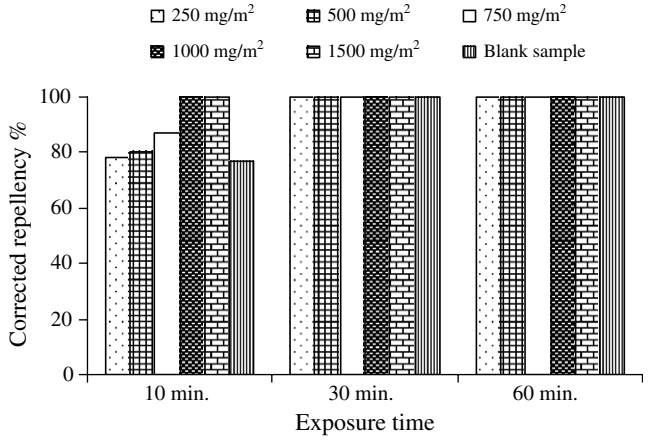

Fig. 4. Relation between prallethrin doses-treated finished fabrics and corrected repellency % at different exposure times. MCT-β-CD-finished cotton fabrics 19%. Blank sample: cotton fabric treated with prallethrin only (1000 mg/m^2).

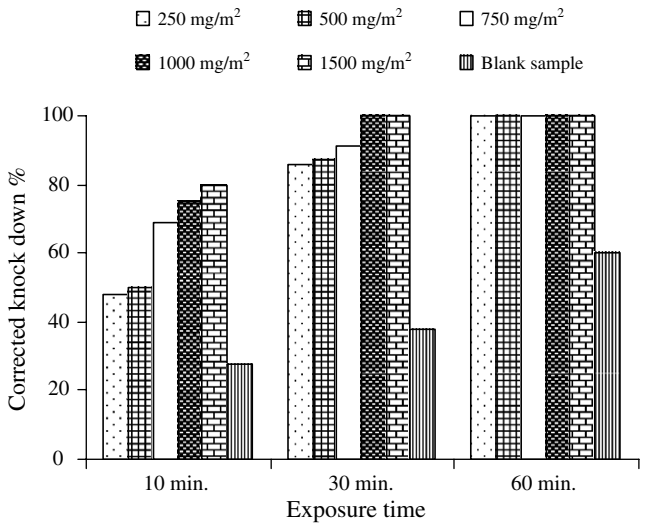

Fig. 5. Relation between prallethrin doses-treated finished fabrics and corrected knockdown % at different exposure times. MCT-β-CD-finished cotton fabrics 19%. Blank sample: cotton fabric treated with prallethrin only (1000 mg/m^2).

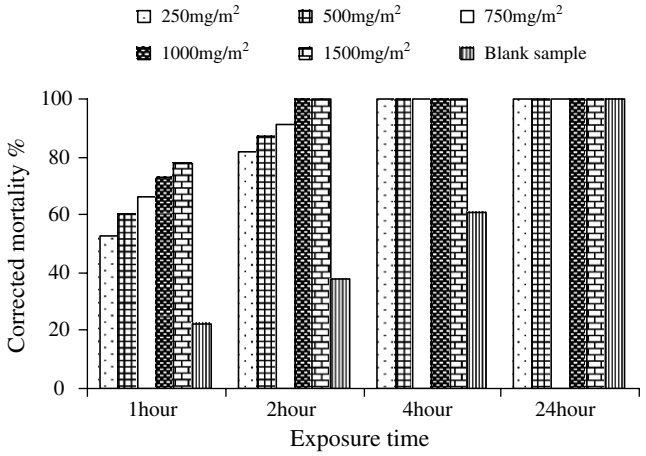

Fig. 6. Relation between bioallethrin doses-treated finished fabrics and corrected mortality % at different exposure times. MCT-β-CD-finished cotton fabrics 19%. Blank sample: cotton fabric treated with prallethrin only (1000 mg/m^2).

and 60 min, whereas for mortality test the time intervals are 1, 2, 4 and 24 h.

Bioassay results in Figs. 1–3 show the toxic activity of MCT-β-CD-finished cotton fabrics treated with different doses of cypermethrin and also show the effect of exposure time against mosquitoes. The bioassay results (Figs. 1–3) represented as corrected repellency percent, corrected knockdown percent and corrected mortality percent. The results (Figs. 1–3) show that the repellent, knockdown and killing action against mosquitoes, increase by increasing the concentration of cypermethrin in MCT-β-CD-finished cotton fabrics within the range studied (250–1500 mg/m^2). Also, result show that the corrected activity (repellency, knockdown and mortality) increased by increasing the exposure time.

Table 1
Effect of washing on the toxic activity of treated and blank samples

Insecticide used for treatment	Corrected repellency %						Corrected knockdown %						Corrected mortality %					
	Blank sample			Treated sample			Blank sample			Treated sample			Blank sample			Treated sample		
	Before washing	After washing	Retention %	Before washing	After washing	Retention %	Before washing	After washing	Retention %	Before washing	After washing	Retention %	Before washing	After washing	Retention %	Before washing	After washing	Retention %
Cypermethrin	60	38	63	81	66	82	22	13	59	42	30	72	9	5	56	37	24	65
Prallethrin	72	44	61	100	100	100	28	0.0	0.0	75	71	95	22	0.0	0.0	73	68	93

Treated sample: 19% MCT-β-CD-cotton fabric treated with insecticide (1000 mg/m^2).
Blank sample: cotton fabric treated with insecticide only (1000 mg/m^2).
Exposure time: 10 min for repellency and knockdown, and 60 min for mortality test.

Table 2
Residual amounts of insecticide after washing of treated fabrics

Insecticide used	Blank sample			Treated sample		
	Before washing	After washing	Retention %	Before washing	After washing	Retention %
Prallethrin	212	66	31	647	370	55

Treated sample: 19% MCT-β-CD-cotton fabric treated with insecticide (1000 mg/m^2).
Blank sample: cotton fabric treated with insecticide only (1000 mg/m^2).

For MCT-β-CD-finished cotton fabrics treated with prallethrin, the bioassay results (Figs. 4–6) show a significant toxic effect at different doses of prallethrin (250–1500 mg/m^2). The toxic activity of prallethrin against mosquitoes is represented as corrected repellency percent, corrected knockdown percent and corrected mortality. The toxicity of treated samples increase by increasing the concentration of prallethrin in the treated fabrics within the range studied (250–1500 mg/m^2). Also, the values of corrected toxic activity values increase by increasing the exposure time (Figs. 4–6).

The bioassay results of MCT-β-CD-finished cotton fabrics treated with cypermethrin and prallethrin (Figs. 1–6) show that at the beginning of exposure, fast repellency, slower knockdown and killing action. These results can be explained 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.

With the resistant strain, the repellency, knockdown and mortality values of prallethrin-treated fabrics are higher than that of cypermethrin-treated fabrics. Generally, the repellency, knockdown and mortality values of MCT-β-CD-finished cotton fabrics treated with cypermethrin and prallethrin are higher than that of blank samples.

3.2. Efficacy of washing

Effect of washing on bioassay of MCT-β-CD-finished cotton fabrics treated with cypermethrin, prallethrin and blank samples are shown in Table 1.

The bioassay results show that for MCT-β-CD-finished cotton fabrics treated with cypermethrin, the retention percent after washing of the repellent action is 82%, and for knockdown 72%, and 65% for mortality. While, for the blank samples treated with cypermethrin, the retention percent after washing are 63%, 59% and 56% for repellency, knockdown and mortality, respectively.

For using prallethrin, the retention percent after washing, of MCT-β-CD-finished cotton fabrics treated with prallethrin (1000 mg/m^2), reached 100%, 95% and 93% for repellent, knockdown and mortality, respectively. While, the retention percent after washing, of the blank sample treated with prallethrin only (1000 mg/m^2), reached 61%, 0.0% and 0.0% for repellent, knockdown and mortality, respectively.

The measured initial prallethrin quantities of treated and blank samples, obtained before and after washing are depicted in Table 2. The results show that there are great losses of the amount of insecticide in blank samples, where the retention amounts reached to 31% for prallethrin. On the other hand, the retention percent for MCT-β-CD-finished cotton fabrics reached to 55% for prallethrin. For cypermethrin no chemical analysis is available, and the decline in the insecticide can therefore only be judged from the bioassays.

The high amount of insecticides remaining after washing the MCT-β-CD-finished cotton fabrics may be due to traping of insecticides of insecticides into the cavities of CDs moiety. This may be due to the cyclodextrin and insecticide bind to each other to form an inclusion complex, wherein the insecticide acts as a gent molecule nesting in the center of the hydrophobic interior of the cyclodextrin. The inclusion complex binds to fabric and allows the insecticide to remain attached to the fabric, even after repeated washes, thereby prolonging the insecticidal effectiveness of the fabric.

4. Conclusions

For this study we conclude that:

- With untreated fabrics about 90% of mosquitoes were able to survive and pass the test period.
- MCT-β-CD-finished cotton fabrics treated with cypermethrin and prallethrin, show fast repellent action, slower knockdown action and killing action.
- The toxic activity of treated fabrics is more than that for blank sample which are treated with insecticide only.
- The comparative study of washing effect shows that the MCT-β-CD-finished cotton fabrics treated with cypermethrin and prallethrin is more effective than blank sample against mosquitoes.

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