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MOSQUITO REPELLENCY OF POLYESTER NETS TREATED WITH CYCLODEXTRIN/REPELLENT COMPLEXES

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ABSTRACT

Fabric treatments with β-Cyclodextrins (β-CD) have been studied for different applications as nanotechnologycal approaches to achieve functional textiles. In particular, repellents and insecticides have been incorporated in β-CD treated textiles to prolong their release. In this case, Citriodiol®, a naturally derived mosquito repellent, was incorporated to β-CD treated polyester (PET) nets. Two methods for citriodiol inclusion were studied; i) pipette dripping or ii) impregnation of fabric in a plastic bag, in order to increase the repellent activity of PET textile substrates. Release profiles were analyzed by gas chromatography and repellency was monitored by in vivo assays with *Aedes aegypti* mosquitoes. Long lasting and reloadable mosquito repellent nets could be achieved by treating PET knits with citriodiol/β-CD complexes.

KEYWORDS

β-cyclodextrin; polyester; mosquito repellency; citriodiol.

1. INTRODUCTION

Mosquitoes are insects of major public health concern because many species are vectors of diseases. Because of global warming the distribution of mosquitoes has expanded from tropical regions to southern latitudes, which has spread the sources of viral infection from mosquitoes. *Aedes aegypti* is the primary vector of dengue, the most important arboviral human infection worldwide. A dramatic increase in the number of dengue outbreaks has been reported in recent years (Dick et al., 2012). The urgent need for global actions to avoid further disease spread has led many researchers to focus on different strategies for the control of mosquito bites.

Bed net impregnation with synthetic pyrethroid insecticides is a wide spread strategy for vector control. The challenge is to protect the user from mosquito bites using mosquito biorepellents.

Citriodiol® is one of the World Health Organization (WHO) recommended repellents for use on skin and clothing. It has been tested and registered by the Environmental Protection Agency (EPA) and included in the European Biocidal Products Directive (BPD) 98/8/EC. It is a naturally derived mixture of substances and can be obtained from eucalyptus citriodiora oil as previously described (Drapeau et al., 2011).

Cyclodextrins are cyclic oligosacharides which can form complexes with host molecules, acting as reservoir of functional agents. If a mosquito repellent forms a complex with β-Cyclodextrin molecules (β-CD), it could be gradually released, prolonging its effect and offering the possibility of reloading the β-CD once the repellent is released. Permanent fixation of β-CD on textile substrates could enable the reload of the

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functional agent even after consecutive washing cycles, providing longer lasting protection against mosquito bites.

In a previous work we demonstrated that polyester knits treated with 15 % w/w β-CD and citric acid resisted at least 6 washing cycles and citriodiol release could be prolonged for at least 7 days (Topollan et al., 2014). In this case, citriodiol was incorporated into β-CD treated polyester (PET) nets by pipette dripping and by impregnation in a plastic bag, as recommended by WHO guides (Leake, 1998). Release profiles were analyzed by gas chromatography and repellent activity was monitored by *in vivo* assays with Aedes aegypti mosquitoes. The aim of this work is to evaluate different methods intended to increase the repellent activity of PET textile substrates by treating them with citriodiol/β-CD complexes for the development of long lasting and reloadable mosquito repellent curtains.

2. MATERIALS AND METHODS

2.1. Textile treatment and evaluation

Polyester (poly(ethyleneterephtalate) (PET) warp knits with a specific weight of 83 g/m^2 provided by Spenco S.R.L., Argentina were treated by impregnation with an aqueous solution containing β-CD (Kleptose®, Roquette, France), citric acid (CA) (Biopack, Argentina) and sodium hypophosphite (SHPI) (Biopack, Argentina) used as a catalyst. Citriodiol® (Citrefine, UK) was used as mosquito repellent.

Impregnation of β-CD was achieved in a lab scale Mathis foulard by nipping to obtain a wet pick up of 100% with an aqueous bath containing 8% w/w of β-CD, 6% w/w of CA and 3% w/w of SHPI (Voncina et al, 2009). Samples were dried and cured in a Mathis tenter frame at 60ºC during 3 min and at 160ºC during 10 min respectively, and rinsed with water at 40ºC during 35 min to remove unreacted reagents. The initial content and grafting yield of β-CD on PET knits was determined by gain in mass (Topollan et al., 2014).

Washing fastness of β-CD on PET knits was tested according to standard ISO 105-C06:1987 using a Gyrowash (James H Heal E Co. Ltd) for 35 minutes at 40ºC. The presence of β-CD molecules on the textile substrate before and after several washing cycles was determined by dropping 20µl of an ethanol-KOH solution of phenolphthalein on each sample. Phenolphtalein forms an inclusion complex with β-CD, presenting a change in the color from pink for untreated textiles to colorless for the CA/β-CD treated textile materials (Dehabadi et al., 2014). The pH of washed samples was determined according to standard ISO 3071:2005, to assure that the change in color of phenolphtalein is due to complexation with β-CD and not to the conformation change at acidic pH.

Two methods for citriodiol inclusion on CA/β-CD treated textiles were studied, namely i) pipette dripping (P) or ii) impregnation of PET knit in a plastic bag (B) (Leake, 1998). Citriodiol was dissolved in a water/ethanol mixture (6:4) to the concentration required to keep a 1.4:1 citriodiol/β-CD molar ratio, i) Solution was dripped in β-CD treated samples with a pipette (1:1 liquid ratio); ii) A plastic bag was filled with the solution (1:0.5 liquid ratio), samples were put into the bag, which was sealed, shaked and kneaded vigorously for 10 minutes, and then removed. β-CD untreated PET knits were used as control. After inclusion, fabrics were dried in the open air during the period of assay.

Citriodiol was extracted from β-CD treated and untreated textiles by incubating a 1g sample with 30ml ethanol for 12 hours at room temperature in closed vials. Citriodiol content in ethanol extracts was determined by gas chromatography with mass detection (GC-MS) in a Shimadzu 2010 coupled to an MS QP2010 detector.

2.2. Repellency test procedure

Repellency to *Aedes aegypti* mosquitoes was assayed for four different conditions, i) untreated PET knits used as blank, ii) CA/β-CD treated PET knits used as control, iii) untreated textiles with citriodiol solution (UC), and iv) CA/β-CD treated textiles with citriodiol solution (CDC). Gloves were manufactured for the evaluation.

The repellent activity was evaluated by inserting a human hand and arm covered with the gloves into a test chamber (50 x 50 x 50 cm), based on cage tests described in bibliography (Kweka, et al., 2008). The covered arm was kept for five minutes in the test chamber containing approximately 200 *A. aegypti* adult females which had not been fed for three to seven days. The number of insects landing was counted independently by two observers. The trials were conducted in quintuplicate in five different cages at 26±1 ºC and 80±5% RH with a 5 minute waiting period between replicates.

Repellency percentage was calculated relating the mean number of mosquitoes landing on citriodiol CA/β-CD treated and untreated textiles with respect to mean number of mosquitoes landing on untreated textiles.

3. RESULTS AND DISCUSSION

3.1. Characterization of β-CD treated PET knits

The final content of β-CD on impregnated PET knits was verified by gain in mass. A 15 % w/w β-CD was obtained with a 30% w/w grafting yield (Topollan et al., 2014). Martel et al. have evidenced that β-CD are grafted to PET knits through the formation of a crosslinked copolymer between CA and β-CD. This copolymer is physically adhered to the fibrous network so that grafting is permanent (Martel et al., 2002). CA/β-CD treated PET knits treated under the described conditions resisted up to 10 washing cycles (Fig. 1). Phenolphtalein solution added to an untreated PET knit shows the characteristic pink color of an alkaline phenolphthalein solution (Fig 1a). As expected, phenolphthalein turned colorless upon application on once-washed CA/β-CD treated PET with a pH of 8.66 (Fig 1b). After 5 and 10 washing cycles, a slight pink color was observed (Figs 1c and 1d respectively). The pH of treated PET after 5 and 10 washing cycles was 6.67 and 6.78, respectively. Even though pH was similar, the color was more intense for 10 cycles than for 5 cycles, indicating that (i) a certain amount of the β-CD was lost during washing and (ii) that color vanishing is due to complex formation between phenolphthalein and the β-CD present on the PET knit. After 12 washing cycles the pink color appears again (Figure 1d), due to the lack of enough β-CD sites on PET available for complex formation.

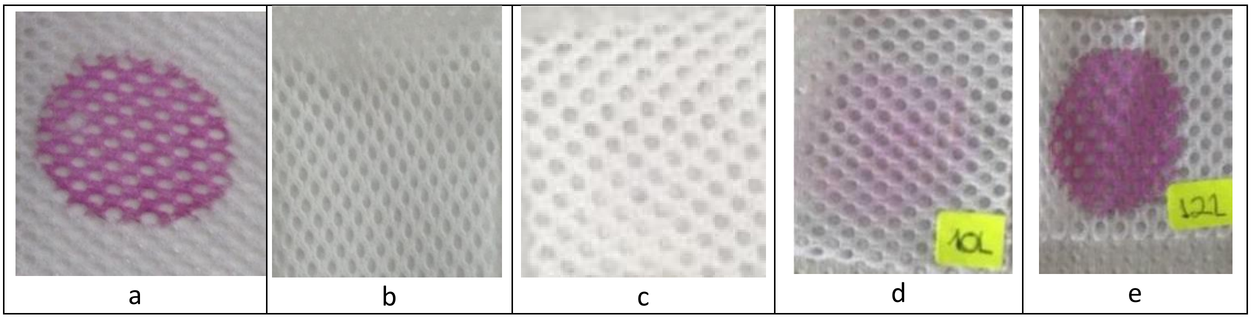

Figure 1: Assays for verifying the presence of β-cyclodextrins with phenolphthalein. a) untreated PET, b) PET with β-CD, 1 washing cycle, c) PET with β-CD, 5 washing cycle, d) PET with β-CD, 10 washing cycles, and e) PET with β-CD, 12 washing cycles. Pictures b, c, d and e were taken 30 minutes after phenolphthalein application.

3.2. Citriodiol content on β-CD treated textiles after citriodiol inclusion

Citriodiol solutions were applied to untreated PET and PET knits treated with 15% w/w β-CD. Oil content was determined by GC on the inclusion day and ten days later (Fig. 2). Samples were kept hanged at room temperature during the period of assay.

Both inclusion methods studied presented similar release behavior. Initial content in all samples was close to the theoretical content (5g citriodiol / 100g PET knit), confirming a good efficiency for both methods. Ten days after application, the effect of the citriodiol/β-CD complex turned significant. Citriodiol content was then twice and three times higher for pipette dripping and plastic bag impregnation respectively compared to untreated PET knits.

Plastic bag impregnation seems a more suitable method for citriodiol inclusion. It is an easy method for the reload of β-CD molecules once the repellent agent is released, reducing the contact with the user and the loss of repellent due to inaccurate dripping. Moreover, the lower liquid ratio required (1:0.5 compared to 1:1 for pipette dripping method) implies lower costs.

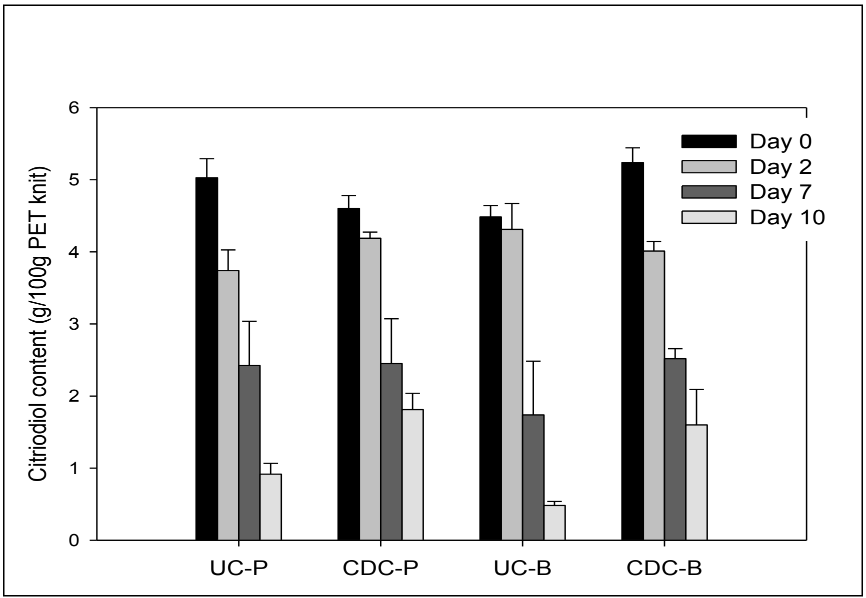

Figure 2: Citriodiol content in β-CD treated and untreated PET. UC-P: untreated PET with citriodiol solution applied by pipette dripping method, CDC-P: CA/β-CD treated PET with citriodiol solution applied by pipette dripping method, UC-B: untreated PET with citriodiol solution applied by plastic bag method, and CDC-B: CA/β-CD treated PET with citriodiol solution applied by plastic bag method. Bars show standard deviations for n = 2

3.3. Repellency tests

Repellency assays against Aedes aegypti mosquitoes indicate that β-CD samples presented only 17±6% repellency on the first day after the treatment. These results show that empty β-CD applied on a textile substrate does not provide protection against mosquito bites. All samples treated with citriodiol provided 100% repellency during eleven days (Fig. 3).

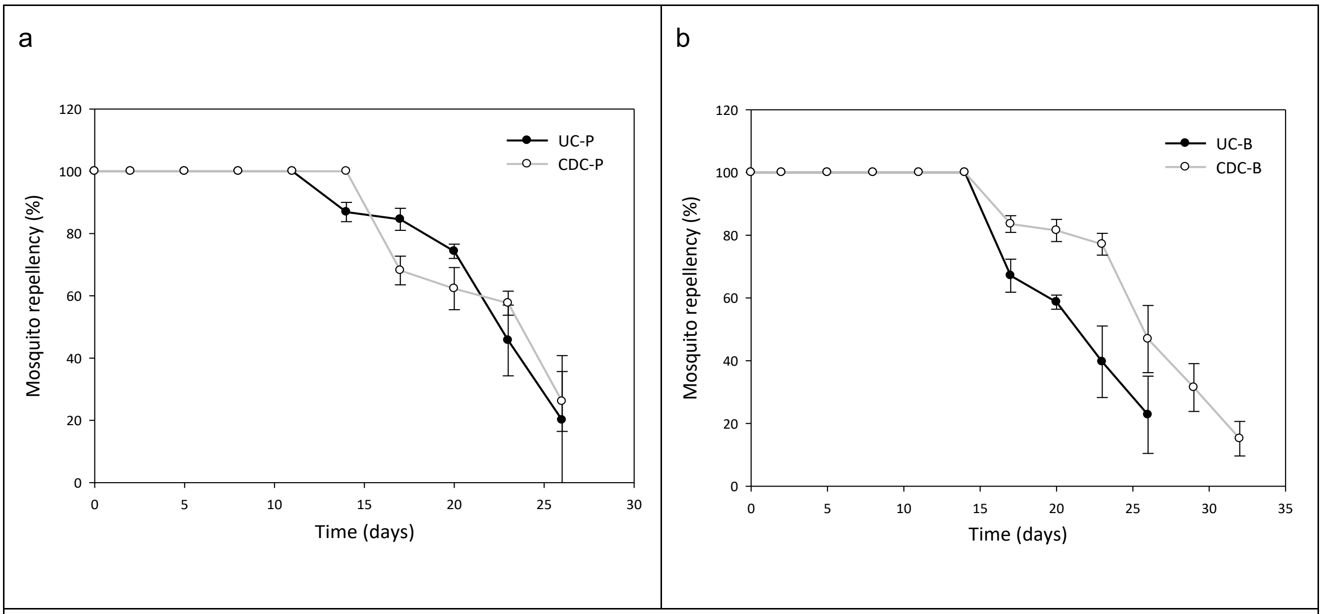

Figure 3: Variation of the repellency percentage as a function of time referred to untreated fabrics. a) UC-P: untreated PET with citriodiol solution applied by pipette dripping method, CDC-P: CA/β-CD treated PET with citriodiol solution applied by pipette dripping method; b) UC-B: untreated PET with citriodiol solution applied by plastic bag method, CDC-B: CA/β-CD treated PET with citriodiol solution applied by plastic bag method. Bars show standard deviations for n = 5

UC-P samples started losing their repellency short before the CDC-P samples (Fig. 3a). However, by day 17th, CDC-P showed just 70% repellency, while UC-P still maintained 85% repellency. This might be due to an inefficient citriodiol/β-CD complex formation accomplished with the pipette dripping method. After day 17th there is no significant difference between β-CD treated and untreated fabric.

UC-B and CDC-B samples showed a different behavior (Fig. 3b). As expected, UC-B samples presented a lower repellency from day 17 on, and this difference increased until day 23. After day 27th there was no significant difference between β-CD treated and untreated fabric. Apparently, the shaking and kneading required for plastic bag impregnation favor the complex formation and consequently delays the release of the repellent agent.

4. CONCLUSION

Foulard impregnation is a suitable method for applying β-CD to PET warp knits enabling the attachment of more than 15% w/w β-CD, and their permanence on the substrate even after 10 washing cycles.

According to the results, plastic bag impregnation would be better than pipette dripping for citriodiol inclusion in CA/β-CD treated PET. Ten days after application, citriodiol content is three times higher in CA/β-CD treated PET that in untreated PET knits. The citriodiol available in both samples is still enough for a high repellent effect (Fig.3).

Repellency results suggest that the complex formation between citriodiol and β-CD is favored by mechanical forces such as the shaking and kneading required for plastic bag impregnation. Even when the scale-up of this method is still to be developed, citriodiol can so far be easily and safely applied even by the final user in rural zones. Moreover, the reload of β-CD molecules is possible once the repellent agent is released. The lower liquid ratio required turns the plastic bag method also more convenient in terms of economic costs.

Polyester nets treated with citriodiol/β-CD complexes will go through an open- field test in order to study the impact of these systems in the control of dengue vector in the Northern provinces of Argentina.

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