Studies on Adsorption of lambda-cyhalothrin-EC on Cotton Mosquito Net

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ABSTRACT
The effective management and control of mosquitoes in human living environments especially with treated nets are crucial to minimize vector-borne diseases such as malaria. Pyrethroid, \( \lambda \)-cyhalothrin has been considered a powerful tool in the control of mosquitoes and is therefore incorporated into mosquito net as pesticide, in this study. The adsorptive behavior of the pyrethroid pesticide, \( \lambda \)-cyhalothrin (alpha-cyano-3-phenoxymethyl-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl-cyclopropanecarboxylate) in aqueous solution on cotton fabrics at different treatment times, temperatures, and concentrations are presented in this study. The results show that the Type I isotherm model provides the most favourable description of the adsorption of LCT-EC on the cotton fabrics. \( \lambda \)-cyhalothrin concentrations of 0.10, 0.15 and 0.20 mg in 50 ml distilled water have been found to be adequate for domestication of the adsorption process to treat virgin mosquito nets at 40\(^\circ\)C. A warm solution (40 – 50\(^\circ\)C) of \( \lambda \)-cyhalothrin (LCT-EC) containing 0.10, 0.15 or 0.20mg LCT-EC in distilled water is therefore recommended for treating a 100sq.cm of new mosquito net. The recommended soaking time for efficient adsorption is between 40 – 50 minutes. The nets can be re-impregnated with the pesticides after every six washes because the functions on the nets are not durable to laundering and storage.

INTRODUCTION
Insecticide-Treated Mosquito nets are major tools for malaria control, especially in sub-Sahara Africa, where the information rate of vector diseases is the greatest in the world\(^1\). Insecticide treated nets (ITNs) and Indoor residual spraying (IRS) are the cornerstone of malaria control programmes\(^2\) and high coverage with either of these interventions can result in a dramatic reduction in malaria associated morbidity and mortality\(^3,4\). The success of this tool has contributed towards the optimism that elimination of malaria as a public Health problem in the Africa continent is a feasible objective\(^5\). Unfortunately the public Health pesticide products market has suffered from massive under investment with the result that there have been no new classes of active ingredients available for wide scale public health applications for more than 30
years. Hence the emergence of resistance to the majority of existing insecticides is in danger of undermining the contribution of vector control efforts. Malaria vector control is currently very dependent on a single class of insecticides the pyrethroids. These insecticides are the only class approved for use on insecticide treated nettings and are being increasingly deployed in IRS programmes in Africa. Pyrethroids are also widely used in the control of agricultural pest worldwide. However, the nets have to be treated regularly with insecticides to offer long – lasting and desired protection for people because the functions on the nets are not durable to laundering and storage. Bed nets pretreated with durable functions by textile mills have improved performance over those that are treated by users. The use of pyrethroid insecticides in malaria vector control has increased dramatically in the past decade through the scale up of insecticide treated net distribution programmes and indoor residual spraying campaigns. Inevitably, the major malaria vectors have developed resistance to these insecticides and the resistance alleles are spreading at an exceptionally rapid rate throughout Africa. Although substantial progress has been made on understanding the causes of pyrethroid resistance, remarkably few studies have focused on the epidemiological impact of resistance on current malaria control activities. As we move into the malaria eradication era, it is vital that the implications of insecticide resistance are understood and strategies to mitigate these effects are implemented. There has been a dramatic increase in reports of pyrethroids resistance in malaria in malaria vectors over the past decade, but few studies have addressed the impact this is having on malaria control; controversy still remains about the epidemiological significance of current levels of resistance in Sub – Sahara Africa. Mosquitoes, such as *Anopheles gambiae* in Western and Eastern Africa and *Anopheles funestus* in South Africa, are becoming more resistant to pyrethroids insecticides. The recent failure of insecticide treated nets and the indoor spraying of insecticide to kill or protect against pyrethroid –resistant *Anopheles gambiae* in Southern Benin showed the urgency of finding alternative insecticides and repellents to supplement or replace the widely over used pyrethroids. A recent study of impregnating with N,N – diethyl – meta – toluamide (DEET) repellent revealed some
promising approaches for overcoming the problems. However, DEET is not a powerful mosquito repellant, and it is hard to achieve very durable functions on polyester nets with DEET.

Pyrethroids, are still considered powerful tools in the control of mosquitoes and are intended to be incorporated into textiles. Pyrethroids are a group of synthetic pesticides similar to the pyrethrum, a natural pesticide produced by chrysanthemum flowers and containing pyrethrums and cinerin. About 200 years ago, people in central Asia discovered that the crushed flower of chrysanthemum were toxic to the insects. Pyrethroids insecticides are currently the only chemicals recommended by WHO pesticide scheme (WHOPES) for net impregnation. Pyrethiods slow the kinetic of both activation and inactivation of the voltage sensitive sodium channels (VSSCs) resulting in prolonging the opening of the individual channels. This allows the sodium ions to cross and depolarize the neuronal membrane and cause repetitive discharge and synthetic disturbances leading to the hyper excitatory symptoms of poisoning. Deltamethrin is one of the insecticides recommended by W.H.O for indoor spraying and for treatment of mosquito nets. Indoor residual spray (IRS) with insecticides is the main stay of the malaria control programme and recommended by the WHO. Pyrethroids and Dichlorodiphenyltrichloroethane (DDT) are mostly used and recommended; however pyrethoids with long residual effects such as deltamethrin are preferred. There is no concrete evidence to support efficacy of outdoor residual spraying in vector control and pyrethoids are less useful as an outdoor residual spray because of their accelerated biodegradation in the presence of light and temperature. In 1996, the malaria control programme in KwaZulu Natal switched from using DDT to deltamethrin for indoor spraying. Within four years, reported malaria cases had increased approximately four – fold, and Anopheles funestus, which had previously been eradicated, had reappeared alive from pyrethroid sprayed houses. Bioassays showed that the species was resistant to pyrethoids but susceptible to DDT. The decision to revert to IRS with DDT was accompanied by a decline in malaria cases by 91%. Although a modest but significant reduction in transmission index and malaria reported cases was observed.
on the Island of Bioko on the West Africa Coast, where an IRS campaign with Lambda cyhalothrin failed to curtail an increase in the population density of pyrethroid resistant *Anopheles gambiae*\(^{23,24}\). Another study was conducted in the highland provinces of Burundi, where a vector control programme combining IRS with pyrethroids and ITNs was initiated in 2002 in one of the most malaria affected island provinces, Karuzi. There have been extensive randomized controlled trials in Africa, aimed at investigating the efficacy of ITNs for malaria prevention\(^{25}\) but very few have assessed how pyrethroid resistance might affect the effectiveness of such intervention. In the Korhogo area in the north of Cote d’ Ivoire malaria is endemic\(^{26}\), lambda cyhalothrin – treated nets had a significant impact on the entomological inoculation rate (53% reduction) and on malaria incidence in children under 5 years of age (56% reduction of clinical attacks) compared to control group having no nets\(^{27}\). This was the first clear – cut evidence of ITNs continuing to provide effective personal protection against malaria in an area with a high vector population. Over 50% reduction in the burden of malaria was achieved in Afghan refugee after IRS\(^{28,29}\).

In Southern Benin, a randomized control trial was carried out in a meso endemic area to access the impact of long lasting ITNs scale – up on malaria morbidity in children under five years of age\(^{30}\). An early experimental hut trials of ITNs in Cote d’ivoire showed no apparent difference in the effectiveness of ITNs between two adjacent sites with resistant and susceptible populations of *Anopheles gambiae*\(^{31}\). By contrast, a comparative study of the efficacy of lambda cyhalothrin used for IRS or net treatment in Southern Benin indicated major loss of efficacy associated with pyrethroid resistance in *Anopheles gambiae* compared to the North where this species remains largely susceptible to pyrethroids\(^{32}\).

Another study on Afghan refugee reported reduction in the prevalence of the *Plasmodium falciparum* from 46.9% to 16.3% after spraying of the tents with permethrin\(^{33}\). IRS with Malathion and lambda-cyhalothrin gave a protective efficacy of 66% against *Plasmodium falciparum* in the refuge camp\(^{34}\). Pyrethoids are less effective with resistance against resistant mosquitoes, particularly *Anopheles gambiae*\(^{35,36}\). The
efficacy of pyrethoid treated nets decreases significantly in the presence of pyrethoids resistance\textsuperscript{32}. Though others have reported their continuous efficacy despite presence of Knock down resistance (Kdr) gene\textsuperscript{36}. In an attempt to overcome this problem, the nets can be dually impregnated (pyrethoids) with a synergist or another insecticide\textsuperscript{35,37}. The nets made up of various materials like cotton, nylon, polyester e.t.c have been useful in preventing the mosquitoes to enter through. Impregnated materials such as insecticidal treated plastic sheets tents (ITPSTs) with insecticides impregnated during manufacturing process are also showing better results\textsuperscript{17,18}. Poor retention of the ITNs was observed under the condition where the community engagement was lacking and competing survival priorities existed\textsuperscript{38}. However many studies have reported high retention and use of ITNs\textsuperscript{18}. ITNs have longer residual insecticidal activity and may be effective up to 13 months\textsuperscript{33}. Washing and exposure to high temperatures and sunlight reduces the efficacy of ITNs and requires retreatment at an appropriate interval\textsuperscript{33}.

A research has also been carried out in China to review the adsorption kinetics and isotherms of pesticides (1, 1, 1-chloro-2, 2-Bis (p-chlorophenyl) ethane) on polyester fibres by carrier finishing\textsuperscript{39}, to study the adsorption behavior of this pyrethoid pesticide in aqueous solution on polyester fibres at different treatment times, temperatures and concentration. The second – order model was found to be the most suitable for describing the kinetic diffusion process and the intra-particle diffusion was the rate –controlling process. The Langmuir, Freundlich, and Dubinin-Radushkevich adsorption models were applied to these approaches.

The issue related to ITNs usage amongst the refuge include the initial cost of the net, their availability at the time of need, social acceptance, retention and retreatment of the nets\textsuperscript{20,29,40}. Pyrethroid treated personal clothing have not been used on a large scale among the refugees, possibly due to the cost of repeated impregnation and loss of residual insecticidal activity due to washing\textsuperscript{41}. A study on Somali refugees reduced the odds of malaria by 70%, but required daily treatment with permethrin\textsuperscript{41}. Studies on the soldiers wearing pyrethroid treated dresses have
reported good protection against malaria\textsuperscript{42}. Factory based permethrin impregnated military uniforms retained the residual insecticidal activity even after one hundred washings. In several endemic areas of the world, laboratory and field trials have shown, treated mosquito nets offer better protection than untreated nets. A Study in Zaire reported that the use of insecticide treated nets (ITNs) resulted in a reduction in the number of bites from malaria vector by 94\%\textsuperscript{43}. In Africa alone, over one million children die from malaria every year\textsuperscript{43}. Hence, in 2006, Kenyan government initiated a program to provide 3.4 million treated nets free to young children\textsuperscript{6}. The impacts of pyrethroid – treated nets\textsuperscript{3,14} and indoor residual spraying\textsuperscript{44} are clearly proven and they remain the most commonly advocated means for individuals and communities to tackle their local malaria problems. The successes of ITNs have revitalized interest in vector control as a visible means to reduce malaria burden, even in parts of sub - Sahara Africa where high transmission levels result in extremely stable prevalence, incidence and chemical burden\textsuperscript{45,46}. ITNs protect individuals either by diverting host-seeking vectors to search for a blood meal elsewhere or by killing those that attempt to feed on that person\textsuperscript{47}. In 2007, the World Health Organization (WHO) recommended Lambda-cyhalothrin for application on mosquito nets. The adsorptive behaviour of the pesticide in aqueous solution on cotton fabrics at different treatment times, temperature and concentration is discussed in this study, using the isotherm models to explain the adsortion behaviour of Lambda - cyhalothrin-ec on the mosquito nets made from cotton fabrics. Lambda-cyhalothrin is a chlorotrifluoro derivative of chrysanthemic acid. It consists of the more active pair of cyhalothrin. Its molecular formula is given as;C_{23}H_{19}ClF_{3}NO_{3}. The chemical name is alpha-cyano-3-phenoxybenzyl-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl-cyclopropanecarboxylate. Despite the popularity of insecticides treated nets, there is no enough information regarding the protocol for regular retreatment with the pyrethroid insecticide in order to offer long-lasting and desired protection against malaria. The regular retreatment approach can prevent the failure of insecticide treated nets that occurred in southern Benin. The treatment protocol may help to diminish the capacity of the mosquito to become
resistant as a result of decreased potency of the net after considerable loss of the pesticide from the net. This study is focused on the investigation of the adsorption pattern of Lambda-cyhalothrin-ec on cotton fabrics at various contact time, temperatures, and the pesticide concentrations, to generate optimized adsorption data that would be suitable for impregnating Lambda-cyhalothrin-ec into the cotton mosquito nets at points of use.

MATERIALS AND METHODS
Cotton nets fabrics was obtained from the Kaduna – central market Kaduna. The pesticide Industrial – grade Lambda – cyhalothrin – EC (Attacke) 2.5% was also obtained from same. The insecticide was received and used without further purification.

Distilled water was used throughout the experiment. All glassware used were washed with detergent, rinsed with water, soaked in aqua reager for six hours, cleaned thoroughly with plenty of water and dried in such a manner to ensure that any contamination does not occur.

100 sq. meter size (10cm x 10cm) of the cotton net was cut. Each pieces of net for a particular concentration of pesticide to be worked on, was weighed respectively using an analytical balance (Model: LA 164 B. BRAN (160g/ 0.1mg). The experiments with the weighed nets for a particular working concentration, were repeated with different times, ranging from 10 minutes to 60 minutes. It was done in the manner, Net₁ for 10 minutes, Net₂ for 20 minutes concurrently up to sixty minutes for a particular concentration of LCT – EC in solution. A control solution was prepared (using distilled water without the pesticide) in 50ml volumetric flask. The experiments with the weighed nets for the control solution were repeated with different times ranging from 10 minutes to 60 minutes to check for any effect of adsorption. A 0.1mg/50ml LCT – EC in distilled water was prepared in a 50ml volumetric flask. The solution was quantitatively transferred into a 250ml conical flask. The weighed net was soaked in the solution and shaked carefully for about 3 minutes and allowed to stay for 10 minutes. The net was quickly removed from the solution and dried under an ambient air condition that was free from any form of dust or contaminants. The weight of the net after drying was measured using the analytical balance. The difference in weight when dried after soaking and before soaking was noted.
after the chosen time for the same concentration. The difference in weight indicates the amount of lambda–cyhalothrin-ec adsorbed on the net. This procedure was repeated for the respective adsorption times and the various concentrations of the pesticide. The effect of temperature of solution on adsorption of lambda–cyhalothrin on the net fabrics studied at 40°C, 50°C and 90°C respectively.

RESULTS AND DISCUSSION
Adsorption isotherms have been used in this study to describe the adsorptive capacity of the pesticide, Lambda cyhalothrin–ec (LCT–EC) on cotton fabrics at different times, concentrations, and temperatures. The extent of the surface coverage by the adsorbate (pesticide) on the cotton fabric of mosquito net has also been described. The adsorptive characteristic of the pesticide was established at different temperatures. Temperature ranges of 28, 40, 50 and 90°C were selected to represent domesticable treatment conditions in real life application. Adsorption at 28°C was room temperature condition without heating, while 40 and 50°C represented just warm condition. 90°C was selected to prevent excessive evaporation of the pesticide carrier solvent (water) when simulating boiling condition. Figure 1 shows the adsorption pattern of the pesticide on the cotton fabrics using λ – cyhalothrin concentrations at room temperature (28°C). The initial λ-cyhalothrin concentration of 0.10 mg/50ml showed no uptake of LCT – EC on the cotton fabrics after 60 minutes. But as the concentration increases the uptake capacity of LCT – EC on the cotton fabrics remarkably improved with respect to time. This initial concentration represents no isotherm type. The λ-cyhalothrin concentration of 0.15 mg/50ml showed an uptake at 60 mins and as well represents the type III isotherm. The λ-cyhalothrin concentration of 0.20mg/50ml showed an uptake capacity between 50 mins and 60 mins. The concentration of 0.25mg/50ml showed its uptake between 30 mins and 60 mins with the maximum uptake capacity at 60 mins. Similarly, for the concentration of 0.30mg/50ml the uptake of the LCT-EC on the cotton fabrics was observed between 30 mins and 60 mins but the maximum uptake capacity occurred at 50 mins.

While in the case of the λ-cyhalothrin concentration of 0.35mg/50ml the uptake
was between 10 mins and 60 mins and the maximum uptake capacity occurred at 50 mins.

Although the adsorption of LCT-EC occurred substantially at the various conditions studied, only LCT-EC adsorption that did not exceed 0.15 mg
was considered adequate for domestication because of WHO imposed limit of not more than 0.15 mg of adsorbed pesticide on treated mosquito nets. On this premise, LCT – EC concentrations of 0.1, 1.5 and 0.2 mg (Figure 2) are adequate for domestication of the adsorption process to treat mosquito nets at 40°C. At room temperature (28°C), LCT – EC concentration of 0.2mg (Figure 1) is adequate for domestication.

At 90°C (Figure 4) the recommended LCT – EC concentration for adsorption is 0.1mg. At 90°C, and 40°C and room temperature conditions, optimum uptake of LCT – EC generally occurred between 40 – 50 mins. The λ-cyhalothrin concentration of 0.20mg/50ml, 0.30mg/50ml and 0.35mg/50ml present Type V isotherm while the concentration of 0.25mg/50ml gave a Type II isotherm at room temperature. Figure 2 shows the adsorption pattern of LCT – EC on the cotton fabrics at different times for the different concentrations of λ- cyhalothrin at 40°C. The initial λ-cyhalothrin concentration of 0.1mg/50ml showed an uptake capacity of LCT – EC on the cotton fabrics between 50 mins to 60 mins and as well represents Type I isotherm. As the concentration increases with an increase in temperature the uptake capacity of LCT – EC on the cotton fabrics showed a significant increase with a decrease in time taken for adsorption to occur. This agrees with the study carried out by Zhang et al., (2010). The λ-cyhalothrin concentration of 0.15mg/50ml and 0.20mg/50ml both showed an uptake between 40 to 60 mins and both produced a steady slope of the curve which leads to the maximum adsorption capacity of LCT – EC on the cotton fabrics. Similarly, the concentration of 0.25mg/50ml, 0.30mg/50ml and 0.35mg/50ml showed an uptake of LCT – EC on the cotton fabrics from 10 to 60 mins. But the concentration of 0.35mg/50ml showed a higher uptake at a lesser time compared to the other concentrations. The λ-cyhalothrin concentration of 0.15mg/50ml, 0.20mg/50ml, 0.25mg/50ml and 0.30mg/50ml all presented the Type V isotherm while the concentration of 0.35mg/50ml represents the Type IV isotherm.
Fig. 2 Effect of time on adsorption of λ-Cyhalothrin on mosquito net at 40°C
Figure 3 shows the adsorption pattern of LCT-EC on the cotton fabrics at different concentration of \( \lambda \)-cyhalothrin at 50°C. The initial \( \lambda \)-cyhalothrin concentration of 0.10 mg/50 ml showed an uptake of LCT-EC at 60 mins and as well represents Type III isotherm. The \( \lambda \)-cyhalothrin concentration of 0.15 mg/50 ml showed a constant adsorption all through from 10 mins to 60 mins and this does not represent any standard isotherm type. The \( \lambda \)-cyhalothrin concentration of both 0.2 mg/50 ml and 0.25 mg/50 ml showed the same pattern of adsorption from 10 mins to 60 mins. The maximum adsorption began at 20 mins and maintains a steady slope up till 60 mins. The concentration of 0.30 mg/50 ml showed an uptake at 10 mins and the maximum adsorption was seen at 60 mins but in the case of the concentration of 0.35 mg/50 ml at this same temperature the uptake of the LCT-EC began at 10 mins as well but the maximum uptake was observed at a lesser time which is at 40 mins. The results produced different isotherms as well. The \( \lambda \)-cyhalothrin concentration of 0.20 mg/50 ml and 0.25 mg/50 ml both represent Type I isotherm. The concentration of 0.30 mg/50 ml gave a Type III isotherm while the concentration of 0.35 mg/50 ml gave a Type IV isotherm.

Figure 4 shows the adsorption pattern of LCT-EC on the cotton fabrics at different times for the different concentrations of \( \lambda \)-cyhalothrin at 90°C. The initial \( \lambda \)-cyhalothrin concentration of 0.10 mg/50 ml showed an uptake capacity between 50 mins and 60 mins. The concentration of 0.20 mg/50 ml showed an uptake of LCT-EC on the cotton fabrics from 10 to 60 mins with the maximum uptake capacity between 30 mins to 60 mins. The concentration of 0.25 mg/50 ml showed an uptake from 10 mins to 60 mins and the maximum uptake capacity was seen between 50 mins to 60 mins. The concentration of 0.30 mg/50 ml showed an uptake from 10 mins to 60 mins but the maximum uptake began from 30 mins to 60 mins with a steady maximum adsorption as described by the isotherm while the \( \lambda \)-cyhalothrin concentration of 0.35 mg/50 \( \lambda \) ml gave equal uptake time but the maximum uptake capacity was observed from 20 mins to 60 mins. Both \( \lambda \)-cyhalothrin concentrations of 0.10 mg/50 ml and 0.35 mg/50 ml produced Type I isotherm. The concentrations of 0.15 mg/50 ml, 0.20 mg/50 ml and
0.30mg/50ml produced the Type V isotherm while the concentration of 0.25mg/50ml gave the Type IV isotherm.

Fig. 3 Effect of time on adsorption of λ-Cyhalothrin on mosquito net at 50°C
Fig. 4: Effect of time on adsorption of \( \lambda \)-Cyhalothrin on mosquito net at 90°C
CONCLUSION
The amount of adsorption of LCT-EC on the cotton fabrics determines the efficacy of the mosquito repellency or kills performance of the mosquito nets. Both the treatment temperature and time were important factors affecting the adsorption processes as they influenced the amount of LCT-EC adsorbed on the cotton fabrics. From the results of this study, adsorption of λ-cyhalothrin to mosquito net is feasible and domesticable. A warm solution (40 – 50°C) of λ-cyhalothrin containing 0.10, 0.15 or 0.2 mg/50ml LCT-EC in distilled water is adequate for treating a 100sq.cm of new mosquito net. The recommended soaking time for efficient adsorption is between 40 – 60 minutes. The nets can be re-impregnated with the pesticides after every six washes because the functions on the nets are not durable to laundering and storage.

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