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An Imidazoline Derivative Functionalized Cotton Fabric for Pesticide Protective Clothing

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Protective cotton clothing at the time of spraying of the pesticides in the agricultural field for the application is very much essential. In the present work, a simple approach was applied to make the cotton fabric with enhanced pesticide protection. A twill fabric and the same fabric subjected to raising operation were functionalized with 1,3-dimethylol-4,5-dihydroxy-2-imidazolidone followed by chlorination with sodium hypochlorite to detoxify the pesticide on its absorption in the fabric. The study was carried out in a newly defined test equipment and using pesticides borne air. An organophosphate pesticide, dimethoate was used for testing. Analysis indicated detoxification of pesticide and the extent of detoxification depended on the chlorine content in the fabric. There was also reduced penetration of pesticide through the fabric. Raised fabrics gave better performance than the unraised fabric. Wet conditions were verified to enhance detoxification.

Key Words: Protective cotton clothing, Pesticides, Detoxification, Dimethoate.

INTRODUCTION

The use of pesticides in agriculture is inevitable[1]. The toxicity of these pesticides varies from slightly hazardous to extremely hazardous[2]. Exposure of human beings to pesticides can occur through inhalation, ingestion and dermal means[3]. When pesticide applicators are considered, they are most commonly affected by dermal route as a result of splash, spill or drift while mixing, loading or application of pesticides[4]. As per the environmental protection agency's estimate around 300,000 farm labourers suffer from pesticide poisonings annually[5]. These poisonings can produce mild to acute and chronic health disorders[6]. Hence, protection of pesticide applicators from pesticide exposure is highly essential. An effective method of protecting these vulnerable people is to provide them user friendly protective clothing. Many of the protective clothing developed are basically from chemical resistant materials, which do not allow permeation and respiration at the same time and generates undesirable effects like heat stress and physical discomfort, especially on the applicators in tropical regions[7]. The only way to overcome such problems is to go for clothing made up of cotton or cotton-rich fabrics. When such fabrics are used by pesticide applicators at the time of spraying, they cannot provide complete protection to them and the extent of protection derived would depend on various fabric specifications. If pesticide applicators are to be protected in a better way, still allowing them to use clothing made up of cotton fabrics, they should be improved without compromising much on their inherent qualities. Attempts have been made by researchers to deactivate or detoxify the pesticides when it comes in contact with cotton clothing through halamine chemistry[8]. A number of *N*-halamine compounds were claimed to have abilities to detoxify carbamate pesticides, especially those having thio and >C=N- groups[9]. Ko *et al.*[8] reported that functionalization of cotton with patented 1,3-dimethylol 5,5-dimethyl hydantoin (DMDMH) followed by chlorination using sodium hypochlorite was able to detoxify carbamate pesticides namely, methomyl and aldicarb effectively. Further, they have stated that the pesticide protective clothing developed from such fabric (halamine cellulosic material) is regenerable in the sense that after the exposure of the fabric to pesticide, it can be reused after washing by subjecting it to chlorination again.

In the present study, an attempt was taken to investigate the effectiveness of 1,3-dimethylol-4,5-dihydroxy-2-imidazolidone (also known as 1,3-dimethylol-4,5-dihydroxy ethylene urea; DMDHEU) in the place of DMDMH against dimethoate (Fig. 1), an organophosphate pesticide, since most of this classification of insecticide possess sulphur and nitrogen centers, as in the case of certain carbamate pesticides considered by Ko *et al.*[8]. It is also a widely used finishing chemical for crease proofing of cotton textiles in the textile industry. The study was conducted on a medium weight cotton woven fabric and the same fabric subjected to a mechanical finish namely, raising. After functionalizing the fabrics with DMDHEU followed by

chlorination, they were exposed to pesticide borne air in a test equipment specially developed for the purpose. The treated fabrics were exposed to pesticide in the equipment both in dry and wet state. Fabrics in the latter state were considered to account for wetting by sweat secreted by the applicators during spraying.

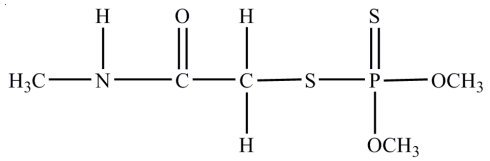


Fig. 1. Chemical structure of dimethoate

EXPERIMENTAL

The specifications of the cotton fabric chosen were as follows: twill weave, 30 × 20 Ne, 49 × 26 yarns/cm and 195 g/m^2. The grey fabric procured was thoroughly desized and scoured before put into use. Raising of the fabric was carried out using a single acting raising machine on the face side (RFS) as well as on both the sides (RBS) taking enough precautions to contain the strength loss within 5 % on either direction of the fabric.

Functionalization: The fabrics (control and raised) were treated separetely with DMDHEU (Arkofix® NDF liq c, Clariant Chemicals (India), Limited, Chennai) with 3 different concentrations 50, 70 and 90 mL/L and adjusting the wet pick-up to 65 % odwm (on the bone dry weight of the material) using 1/3 volume of DMDHEU of 6 % w/v $MgCl_2$ LR (Qualigens fine chemicals Pvt. Ltd. India) as catalyst. The padded fabrics were then dried at 80 ºC for 6 min and cured at 120 ºC for 7 min. After thoroughly washing and drying, the treated fabrics was chlorinated using sodium hypochlorite with 4 % available chlorine content (Qualigens Fine Chemicals Pvt. Ltd., India) using concentrations 0.5, 1 and 2 gpl for 1 h at pH 11. These fabrics were then subjected to antichlor treatment with 2 % owm (on the weight of the material) sodium sulphite LR (Qualigens Fine Chemicals Pvt. Ltd., India) at room temperature for 30 min using liquor to material ratio of 50:1 to eliminate free chlorine content. After thorough washing and drying, these functionalized samples were taken for estimation of available chlorine content following the test method IS 2350-1963. Three samples each from control and raised functionalized fabrics with wide difference in available chlorine content were chosen and considered for further studies.

Exposure to pesticide: Contact of pesticide with the control and raised, both untreated and functionalized samples in bone dry state was made using a test equipment (Fig. 2) specially developed by the authors to evaluate the performance behaviour of all kinds of protective fabrics to be used by the pesticide applicators at the time of spraying. This equipment can generate pesticide borne air of required qualities. In the present study, the air with following specifications was generated and used on fabric samples with an effective exposure area of 0.5 cm^2: contact velocity -6.5 km/h, pesticide concentration - 1 mg/m^3, moisture content -0.34 kg/kg of air and temperature 29 ± 1 ºC. The samples were kept in the sample holding device of the test equipment backed up with Benchkote plus absorbent paper (Whatmann 2301-6150). When this set up is exposed to pesticide borne air for certain duration, the amount of pesticide present in the fabric will give its absorption behaviour and that in the absorbent paper will give the penetration of pesticide through the fabric out of the total quantity of pesticide that has come in contact with the set up. In the present work, exposure duration of 1 h was used. The exposed control and raised fabrics, both untreated and functionalized and their respective absorbent papers were extracted following ASTM 2130-01 method using HPLC grade acetone (Merck Specialities Pvt. Ltd., India). It was followed by concentrating the extracted volume to 5 mL using a rotary evaporator (Buchirotvapour R-215, Switzerland) and its concentration was found out using gas chromatography (GC) (Shimadzu GC 2010) having flame photometric detector. % Absorption per hour and % penetration per hour were calculated from dimethoate absorbed by the fabric and paper respectively using the average value obtained from the two samples. The best performing control and raised fabrics from the above were chosen to conduct studies on the effect of wetting. The moisture content in these fabrics were adjusted to 25, 50 and 75 % odwm using padding mangle. After exposing them to pesticide borne air in the test equipment, they were dried at ambient conditions and taken for determination of pesticide absorption and penetration following the procedure given above. Two specimens were considered for every sample. Using the average of these values, % decrease in absorption and penetration over the dry fabrics were calculated for both control and raised fabrics.

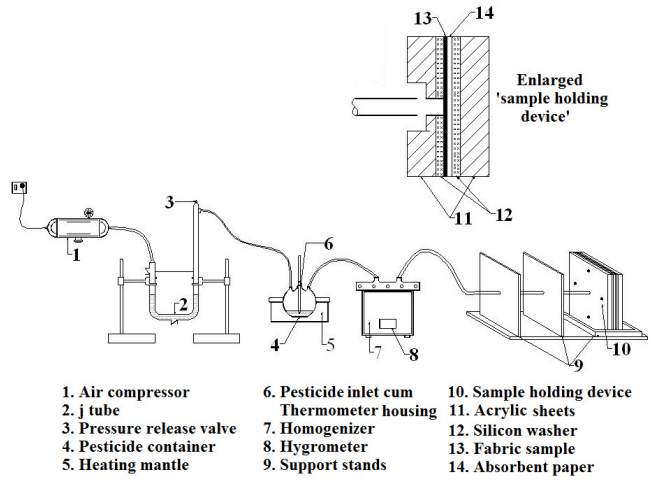


Fig. 2. Test equipment

RESULTS AND DISCUSSION

Effect of functionalization: The functionalized fabrics with chlorine content 0.02, 0.07 and 0.12 % were chosen. The effect of chlorine content on absorption and penetration of pesticide is given in Fig. 3. It can be observed from the plots that the presence of chlorine decreases the absorption and penetration of pesticide and this trend increases as the chlorine content increases. The decrease in absorption values shows that the functionalized fabrics are able to detoxify the pesticide. Since the pesticide undergoes detoxification during absorption, the effective quantity of pesticide available for penetration through the fabric decreases. Hence, as the absorption decreases, penetration also decreases. The penetration values obtained

for raised fabrics are lesser than that of the control fabric. Hence, the raising operation assists in better detoxification of the fabric. Both side raised fabric gives higher performance than face side raised fabric. The proposed mechanism of detoxification is presented in **Scheme-I**.

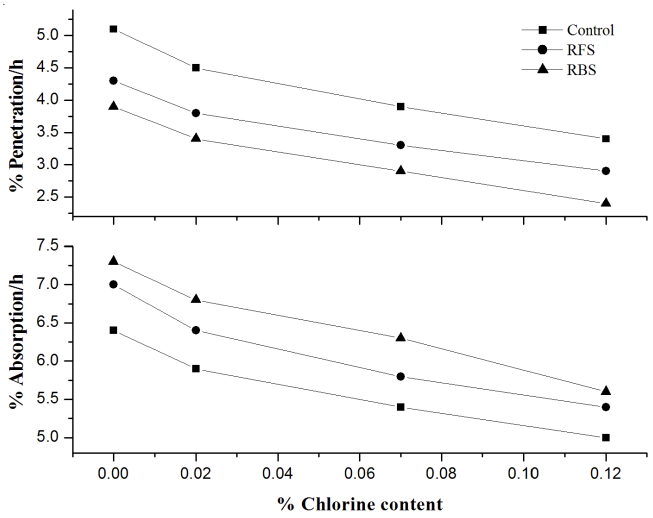
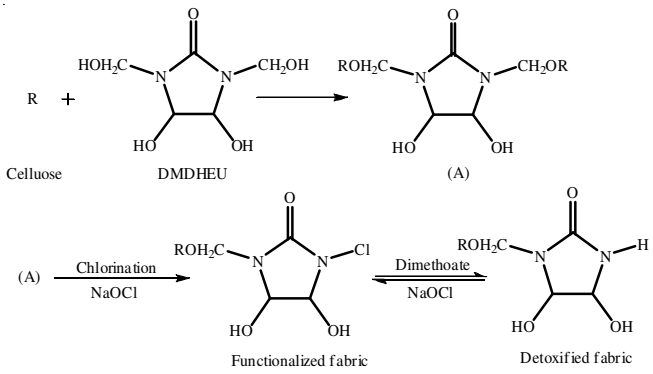


Fig. 3. Effect of chlorine content on pesticide absorption and penetration



Scheme-I: Proposed mechanism of detoxification

The electrons released from the methoxy groups in the pesticide molecule via the resonance build high electron density on both the sulphur centers in it ease the oxidation of them by the chlorine released from the functionalized cellulose. Similarly, the amide nitrogen present in the molecule is also susceptible to oxidation by the halogen, as it carries electron releasing methyl group. Further, in the GC analysis carried out to estimate pesticide absorption and penetration, no newer fragments were detected. Hence, it can be stated that the pesticide might have undergone complete mineralization due to oxidation to form CO_2, H_2O, SO_4^{2-}, NO_3^- and PO_4^{3-} resulting in its detoxification. For the regeneration of functionalized fabric, the detoxified fabric has to be treated again with sodium hypochlorite.

Effect of wetting on detoxification: Among the various functionalized fabrics in dry state studied, the fabrics with 0.12 % chlorine content rendered maximum detoxification. These fabrics were considered for wetting studies. Wetting of the functionalized control and raised fabrics is found to decrease the absorption and penetration of the pesticide. The effect of wet pick-up levels on % decrease in absorption and penetration of these fabrics over the respective bone dry functionalized fabric is given in Fig. 4. It can be seen from the figure that as the wet pick-up increases the extent of decrease also increases. In all the fabrics, the extent of decrease is maximum at lowest wet pick-up level considered. It shows that unbound water has got lesser degree of role to play compared to bound water in deciding the performance behaviour of the fabric.

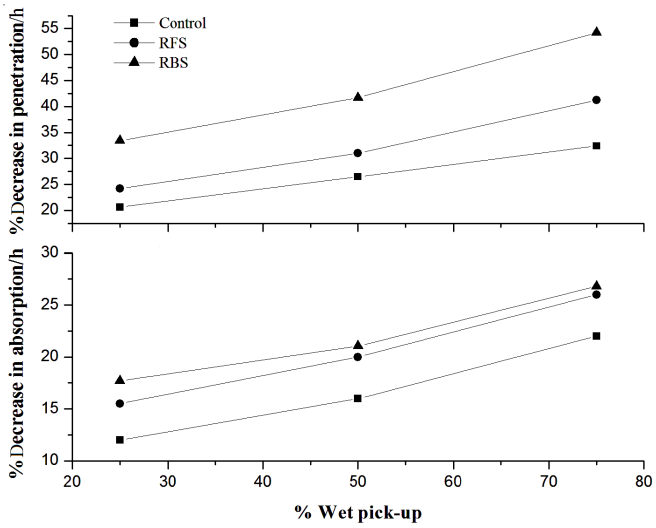


Fig. 4. Effect of wet pick-up levels on pesticide absorption and penetration

Conclusion

Functionalization of the cotton fabric with dimethylol-4,5-dihydroxy-2-imidazolidone followed by chlorination is found to detoxify sulphur and nitrogen containing organophosphate pesticide, dimethoate. Detoxification results in decrease in the pesticide penetration through the fabrics. Wetting of control and raised fabrics further increases the detoxification and decreases the penetration of pesticide and higher the level of wetting better is the detoxification and lower is the penetration. Thus, it can be said that functionalized both side raised cotton fabric is the best one for the preparation of protective clothing which would give protection to the applicators from pesticide.

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