Reduction of organophosphate insecticide residues in agricultural product using hydrophobic deep eutectic solvents based DL-Menthol

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Abstract. Agricultural products, such as tomatoe, still contain insecticide residues that are harmful to humans as well as the environment. The commonly used insecticide is the organophosphate, where the residue are poisonous to the plant environment even to humans. Hydrophobic Deep Eutectic Solvent (DES) is a new generation of nonpolar solvent from ionic solvents because it has better physical properties and solvent properties for the extraction process. In this study, DES was synthesized at 50 ºC for 15 minutes with a stirring speed of 300 rpm and a molar ratio of DL-menthol: lauric acid varied from 1: 1, 2: 1, and 3: 1. Tomatoe from agricultural product, washed with DES mixed with 200 ml aquadest and washed with running water. DES characteristics are analyzing the shape and measuring freezing point, density and viscosity. The concentration of pesticide residues was analyzed using Gas Chromatography-Mass Spectrometer (GC-MS). Dimethoate insecticide removal is better using hydrophobic DES with a molar ratio of 3: 1, while the insecticide residue can be accessed reaching 46.25%. And for the Chlorpyrifos and Profenophos insecticide is better to use water, while the Chlorpyrifos and Profenophos insecticide residues can be reduced to reach 25.87% and 75.40%.

1. Introduction

Indonesian agriculture is one of sectors that important in the national economy, agriculture sector is the main sector providing food for 245 million people in Indonesia and about 87% of raw materials of small and medium industries. Agriculture also contributing about 15% of gross domestic product (GDP) and become a major source of income for about 70% of households in rural areas. For improving the crop production, farmers minimizing the development of pests like insects and fungi by using pesticide. In Indonesia, the number of registered pesticides has grown from 1557 in 2006 to 2628 in 2010 [1,2]. Most of developing country especially in Indonesia, use organophosphates (OPs) insecticide to protect crops from pests. OPs application is still the most effective and accepted means for the protection of plants, and has contributed significantly to enhanced agricultural productivity [3].

The use of pesticides not only increases crop yield but it may also have negative impacts for producers and also consumers. Globally, about 25 million farmers experience accidentally pesticide poisonings each year, and it is estimated that approximately 1.8 billion people work in agriculture and most use pesticides to protect food and commercial products that they produce. Farmers have not good knowledges of pesticide selection, timing of application and harvesting period that important to avoid health risks. They also use unsafe storage facilities, ignore risks and safety instructions, and do not use protective devices when applying pesticides [4,5]. The majority consumers get impacts mostly from low OPs concentration residues in foods. Short-term effects of exposure to these chemicals have been studied
mostly in the nervous system, which is the main target. For the long-term, exposure these chemicals effect on the immune system, reproductivity, body tissue, and could affect a variety of cancers through an immunological mechanism [6].

There are some several methods for removal pesticides from agricultural products such as washing with running water [7], washing with mixture of water and ozone [8], soaking with hot water [9], pH control [10], and using ultrasonic radiation [11]. Challenge in the future is to find method with high efficiency of reduce pesticides especially pesticide that often used in developing country, keep nutrients of product and safety to use. Because the methods have been studied before only reduce certain types of pesticide and need more further research about product’s condition after used those methods.

Deep Eutectic Solvents (DESs) are defined as a mixture of two or more components, which may be liquid or solid and at a particular composition present a high melting point depression, becoming liquids at room temperature. By definition, DESs consists of hydrogen bond donors (HBDs) like free fatty acid and Hydrogen Bond Acceptors (HBAs) like ammonium salt, which rendering a new chemical entity with a melting point lower than of the initial compounds. DESs have comparable characteristics to ionic liquids (ILs), but DESs have some advantages than ILs such as less toxic, lower cost of the raw materials, and often biodegradable[12,13]. Most of the DESs proposed so far have a hydrophilic character and thus are unstable in water, leading to the seperation of both component. Hydrophobic DES is the new class of DESs with better characteristics than hydrophilic and ILs. The water-immiscible characteristic from hydrophobic DESs offer an advantage in many liquid-liquid extraction process. There is research that used hydrophobic DESs for extraction of pesticides from aqueous environments with good result of extraction efficiency [14,15].

In this study, we give another step in the development and understanding of hydrophobic DESs function for removal OPs residues from agricultural product. For that purpose, hydrophobic DES based DL-Menthol as HBAs were combined with lauric acid as HBDs with several different rasio molars. Efficiency extractions obtained from concentration agricultural product before and after washed with mixture of hydrophobic DESs and water. The attained results were compared with those obtained when only water were used.

2. Materials and Methods
2.1 Materials
Agricultural product that used for this study is fresh Tomatoes from Tanah Karo, North Sumatera, Indonesia. The tomatoes round and weighing approximately 100 to 110 g each were took from the farmer. For the last 3 months, the farmer used some organophosphate insecticides that contain dimethoat, chlorpirifos, and profenofos with unknown concentration. To determine the concentration of pesticides, pesticide residue analysis was carried out by using gas chromatography.

| Agricultural Product | Pesticide | Concentration (mg/kg) |
|----------------------|-----------|-----------------------|
| Tomatoes             | Dimetoat  | 0.387                 |
|                      | Klorpirifos| 0.491                 |
|                      | Profenofos| 0.756                 |

For hydrophobic DESs compositions, DL-Menthol (purify ≥ 95%) as HBAs and lauric acid (purify ≥ 98%) were purchased from Sigma-Aldrich.
2.2 Preparation of hydrophobic DESs

All DESs were prepared according to the previous methodology [14,16], by heating and mixing the two compounds (HBA and HBD) with different molar ratio HBA:HBD. DL-menthol based eutectic mixture was prepared by adding lauric acid to DL-menthol with the following molar ratios : 1:1 (DES 1), 2:1 (DES 2), and 3:1 (DES 3). The mixture of the two compounds was then heated using hot plate (Thermo Scientific) up to 50 °C for 15 min and stirring speed 300 rpm. After the mixture homogenous, cooled down slowly until it reaches the room temperature.

2.3 Washing treatments

Nine hundred to 1,000 g of Tomatoes were washed with DESs solution and fresh tap water. About 500 g Tomatoes were washed with DESs solution. 5 ml of DESs solution are mixed with 200 ml of aquaest in beaker glass 500 ml and afterward used the solution to wash tomatoes for 2 minutes each Tomatoe. The rest of the Tomatoes were washed with fresh tap water for 5 minutes each Tomateo [7]. To determine the concentration of pesticides, pesticide residue analysis was carried out by using gas chromatography.

2.4 GC-MS Analysis

The sample was chopped 15 grams using a knife or a blender. After that, the sample is pulverized with 30 ml Acetone using ultra turaks for 30 seconds. 30 ml dichloromethane and 30 ml petroleum ether 40-60 °C added to the sample and then pulverized again for 30 seconds. Pipette 25 ml organic phase formed from the sample into a boiling flask. And then concentrated with the evaporator at water temperature 40 °C until it is almost dry, the sample dried using nitrogen gas. Dissolve the residue in 5 ml iso octane : toluene (90 : 10, v/v) before tested using GC. Inject 1-2 µL residue and standard solution to gas chromatography. GC is equipped with a specific detector for compounds containing the element phosphorus (FPD and NPD). GC system equipped with capillary column (0,25 mm inside diameter, 0,25 µm film and 30 cm length coloumn). The GC was operated in the constant pressured with coloumn temperature 190 °C, injector temperature 230 °C, and detector temperature 230 °C.

3. Results and Discussions

3.1 Effect of Hydrophobic DESs as Washing Solvent

The pesticide reduction for the organophosphate pesticides using the proposed DESs and fresh tap water are plotted in Figure 1 and in Table 2 is presented the concentration of pesticides after washed with hydrophobic DESs and fresh tap water.

![Figure 1](image_url)

**Figure 1.** Comparison of percentages of pesticide reduction using hydrophobic DESs based DL-Menthol with different ratio molar and using fresh tap water.
Tabel 2. Pesticides Concentration (mg/kg) after washed using hydrophobic DESs and fresh tap water

| Washing Treatment | Pesticide (mg/kg) | Dimethoat | Chlorpirifos | Profenofos |
|-------------------|-------------------|-----------|---------------|------------|
| DES 1             | 0,310             | 0,260     | 0,208         |
| DES 2             | 0,437             | 0,429     | 0,387         |
| DES 3             | 0,447             | 0,425     | 0,346         |
| Fresh Tap Water    | 0,330             | 0,364     | 0,186         |

From Figure 1, it can be observed that in general the pesticide reduction of the studied three pesticides that contain in Tomatoes using hydrophobic DESs is good enough. Pesticide reduction using DES 1 follow the order: Dimethoat (19,89%), Chlorpirifos (10,99%), and Profenofos (40,87%). DES 2 follow the order: Dimethoat (32,82%), Chlorpirifos (12,63%), and Profenofos (43,78%). And using DES 3 follow the order: Dimethoat 46,25%), Chlorpirifos (21,18%), and Profenofos (54,23%). Despite the chemical diversity of these three pesticides, pesticides hydrophobicity is the key for the extraction from sample. Hydrophobic DESs that is synthesized are non-polar and difficult to dissolve in water. Based on the polarity characteristics, non-polar organophosphates molecules are distributed symmetrically and bind to hydrophobic DESs because its polarity so that elimination of pesticides on tomatoes can occurred.

From the result of this study, Dimethoat pesticide reduction is better to use hydrophobic DESs than to use fresh tap water. But for the reduction of Chlorpirifos and Profenofos it is better to use fresh tap water. Although pesticide reduction of Chlorpirifos and Profenofos using fresh tap water is better than hydrophobic DESs, the use of DESs needs to be considered. There are several pesticide reduction factors that still need to be further investigated to optimize the function of hydrophobic DES for pesticide reduction.

3.2 Effect of the molar ratio of DES compounds

The pesticide reduction using hydrophobic DESs affected by the molar ratio of its constituents. Figure 2 is presented the effect of the molar ratio of DES compounds toward pesticide reduction using hydrophobic DESs.

![Figure 2. Effect of the molar ratio of DES compounds toward pesticide reduction](image_url)

From Figure 2, it can be observed molar ratio of DES compounds affect pesticide reduction. Average pesticide using DES 1 (23,92%), DES 2 (29,74%), and DES 3 (40,56%). The increase of HBA (DI-Menthol) in hydrophobic DES causes characteristic changes such as density, viscosity, and
hydrogen bonds. Other than those, increase of molar ratio affect water solubility of hydrophobic DES. Molar ratio of DES compounds could be an important factor in future to optimize pesticide reduction.

4. Conclusions

In this work, the use of hydrophobic DESs in the pesticide reduction of organophosphate pesticides in agricultural product was studied. Hydrophobic DESs based DL-Menthol were synthesized with different molar ratio of its compounds which used as a washing solvent. Fresh Tomatoes that contaminated with OPs such as dimethoat, chlorpirifos and profenofos washed with solvent mixture of water and hydrophobic DES. As a comparison, fresh Tomatoes were washed with fresh tap water. Hydrophobic DESs can reduce pesticide especially Dimethoat with molar ratio of DES compounds 3:1 (DES 3). Despite using fresh tap water is better for pesticide reduction of Chlorpirifos and Profenofos than using hydrophobic DES, hydrophobic DESs need to be considered in the future due its characteristics. This study also obtained effect of molar ratio of hydrophobic DES compounds in the reduction of pesticides, where more DL-Menthol (HBA) in hydrophobic DES then increase pesticide reduction. Further researches needed about the use hydrophobic DES for pesticide reduction, because there are some factors which can improve % pesticide reduction.

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