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PREPARATION AND CHARACTERIZATION OF PALM OIL-BASED LOTIONS FOR ORGANOPHOSPHORUS COMPOUND CONTAMINATED SKIN DECONTAMINATION

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ABSTRACT

Organophosphorus compounds (OPs) are very toxic chemicals and become a major threat to civilians and military personnel as they are commonly used as pesticides and chemical weapons. Since their penetration rates through human skin are relatively high, an immediate decontamination upon dermal exposure is vital and this can be carried out by applying a lotion containing ingredients that react with the OPs to produce harmless products. As an effort to reduce our dependency on foreign technology which becomes a big threat to our country security and budget, we have been exploring of a possibility of producing our own OP reactive skin decontamination lotion. In this report we describe a procedure to prepare a palm oil-based lotion that can be used to as a matrix for incorporating active ingredients to remove OPs from an OP contaminated skin. The pH of the lotion was ranged between 8 to 9 and remained in this range for over 6 months. In addition, there was no phase separation and microbial growth observed when the tests were carried out. The absence of new and major shift of functional groups in the FTIR spectrum of the stored lotion suggested the product was also chemically stable.

1.0 INTRODUCTION

In the last century, chemical warfare agents are derived from synthetic toxic chemicals and biological poisons [1]. In 1915, German used chlorine during the Battle of Ypres, marked the beginning of the chemical warfare era. During World War I, sulphur mustard was immensely used, and the range of concentration was 19 to 33 mg/m^3. Due to the high concentration, an exposure for 30-60 minutes can cause severe injury including deaths [2]. Patients who are exposed to these nerve agents will show the toxic sign in such order: hypersecretions, tremor, convulsions, coma and eventually death caused by paralysis of heart and respiratory distress [3]. In the reference of terrorism attack in few countries, there is handful of bioweapons involved that harm tens of thousands of civilians. This has grown the concern of many scientists in applying the decontaminant strategy to both military as well as civilians. Starting in 2014, at least 37 discrete attacks in Syria and Iraq has utilized chemical weapons during warfare which causing deaths and injuries of numerous non-military people [4]. Though organophosphorus base agents are primarily known as chemical warfare agents, they are also mainly used as pesticides in agricultural industry. Severe accidental poisoning has been reported and caused majority number of deaths globally [5]. Self-poisoning involving organophosphorus has made up to one third of world's suicide which leads to a global concern and appeals for a policy attention [6].

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The major drawback of physically removing the nerve agents is that the substance used, such as water, need to be detoxified and disposed of attentively [7]. Adsorbent powder like flour and talcum powder was used to physically remove the nerve agents from the reactive skin. It is then wiped off using moist paper. It can also be chemically decontaminated by using free chlorine agents such as chloramine powder and dilute hypochlorite solution. M258A1 kit was introduced during World War I for skin decontamination, which consists of a towelette of phenol and hydroxide and also a towelette of chloramine [2]. The solid absorbents bind to the chemical weapon agents, forming a residue to be brushed away. Unfortunately, the adsorbents do not change their chemical make-up. The main disadvantage of this type of decontaminant is that those residues may be inhaled or the desorption of chemical agents from the adsorbents may occur. Joint Services Personnel Decontamination System (JSPDS) has been established in 2004 to innovate an effective skin decontaminant solely for military use. Decontamination of chemical warfare agents and toxins involves two main mechanisms which are physical removal and chemical neutralization by the active ingredients [8]. The idea of incorporating active ingredient in the lotion is not new and has generated significant interest, as proved by abundance of research articles on this topic [9]. Later, JSPDS innovate M291 SDK, a combination of carbonaceous material, as the adsorbent, and two ion exchange resins to neutralize the chemical agents. Yet, the neutralization of resins and the chemical agents is too slow which makes M291 SDK behaves as a non-reactive dry decontaminant.

In 2003, Food and Drug Administration (FDA) has approved reactive skin decontamination lotion (RSDL) as a medical device for the removal and neutralization of chemical weapon agents and certain biological toxins [10]. It is a green wallet-like sleeve consists of lotion impregnated applicator pad or sponge [11]. The RSDL kit is chemically composed of Dekon 139 and 2,3 butanedione monoxime (DAM) in the mixture of ethylene glycol monomethyl ether (PGME) and water [12]. Within the pores of the sponge, high molar of the active ingredients will be rapidly mixed with the chemical warfare agents to accelerate the neutralization of the chemical [13]. Oxime group is used as the reactivator of inhibited acetylcholinesterase (AChE) due to its high nucleophilicity. Nucleophilic site of oxime dephosphorylates the phosphoryl group, allowing the AChE to be reactivated and bind to other acetylcholine [14]. The main objective of our study is to develop an optimal formulation of lotion to be incorporated with active ingredients against organophosphates substances. Selected commercial lotion were included in the study as a reference. The phase stability of emulsion was then monitored for six months by seeing any changes in pH and phase separation.

2.0 MATERIALS AND METHODS

2.1 Materials

Coconut oil, fatty acids, glycerine, preservatives, sodium hydroxide and samples of two commercial lotions were purchased from local retailers (Kuala Lumpur, Malaysia). Palm olein oil was obtained from Sime Darby Sdn. Bhd as a gift.

2.2 Preparation of emulsion

Coconut oil must be warmed beforehand as it separated due to cooling. The ingredients of oil phase were incorporated in a 100 ml beaker and heated on a stirring magnetic plate until melted with a gentle stirring. In another 100 ml beaker, aqueous phase is gentle stirred and warmed at the same time. The aqueous phase is then combined into the oil phase. The emulsion is stirred for 30 minutes while it cools down and homogenized for another 3 minutes. The lotion is put in the refrigerator for 10 minutes and homogenized again for 3 minutes. Preservative and two drops of essential oil are added then to the emulsion and ready to be poured in selected bottles. Table 1 shows the ingredients of each lotion sample that comprises of oil and aqueous phase samples, preservative and essential oil.

Table 1. Ingredient compositions of the prepared lotions

Sample	Lotion 1	Lotion 2	Lotion 3
Oil phase			
Palm olein oil	10.8012 g	12.0002 g	10.8003 g
Coconut oil	8.0054 g	10.0040 g	8.0012 g
Fatty acid	6.0119 g	6. 0030 g	6.0500 g
Emulsifying wax	6.0163 g	6.0056 g	6.0014 g
Aqueous phase			

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Deionized water	94.0010 g	94.0000 g	94.0067 g
Glycerin	1.2517 g	1.2091 g	1.2213 g
Sodium hydroxide	0.1661 g	0.1701 g	0.1680 g
Preservative	-	0.5102 g	0.5005 g
Essential oil	Two drops	Two drops	Two drops

2.3 Phase separation

The prepared lotions were kept at room temperature and the formation of oil and aqueous layers due to phase separation was observed to evaluate the stability of emulsions. The morphology of emulsions was investigated using a digital optical microscopic magnifier. The samples were prepared by direct depositions of emulsions on glass slides.

2.4 pH determination

Readings of pH were measured using HORIBA pH meter after calibrating it with standard solution. pH for each lotion was measured three times and the average pH was recorded. The pH of distilled water used to rinse ranged from 7.0 to 7.4.

2.5 Fourier Transform Infrared (FTIR) analysis

A FTIR spectrometer (Perkin Elmer) coupled to an ATR accessory was used to measure the functional groups in the prepared and commercial lotions. Each sample was directly placed on the ATR crystal surface and the absorbance spectrum was collected. A dry and empty ATR cell was used as a reference. The FTIR spectra were recorded in the range of 4000-600 cm^{-1}. The crystal was cleaned with acetone after every usage.

3.0 RESULTS AND DISCUSSION

There are four different types of emulsion which are water in oil emulsion (W/O – water droplet dispersed in oil phase), oil in water emulsion (O/W – oil droplet dispersed in water phase), water in oil in water (W/O/W) and oil in water in oil (O/W/O). Technical aspects such as t ability or final consistency of emulsion are crucial to contemplate in selecting the type of emulsion [15]. Lotion is an emulsion and appropriate matrix for a decontamination device since it is more to liquid side, therefore, easy to spread to absorb compounds from skin surfaces [16-17].

Emulsions are stable mixtures composed of water, emollient, emulsifying agents, humectants and preservatives. They tend to separate back to their own component oil and aqueous phases over time as they are thermodynamically unstable. Emulsifiers are the main component that hold these two phases from being immiscible. Upon homogenization, multilayers of liquid crystals saturated at the oil-droplet-water interface. These multilayers stabilize the mixture by reducing the London van Der Waals forces of attraction that will delay the coalescence process [18]. In this work, there is no phase separation occurred in all prepared lotion, owing that the consistency of emulsion remains the same and there is no oil and aqueous layer formed in all the prepared lotions over the period of 6 months. Table 2 summarises the colour and the texture of the prepared lotions and comparison with that of the commercially available products. All the products are white in colour with silky smooth textures, same as the commercial product of o/w emulsions.

Table 2. Physical properties of prepared and commercial lotions

Lotion	Colour	Texture	Emulsion type
Lotion 1	White	Silky smooth	o/w
Lotion 2	White	Silky smooth	o/w
Lotion 3	White	Silky smooth	o/w
Commercial 1	White	Buttery	w/o
Commercial 2	White	Silky smooth	o/w

A uniform distribution of the dispersed globules of oil throughout the aqueous phase defines a stable emulsion [19]. To maintain the state that oil droplets are homogenously dispersed in aqueous phase, emulsifiers are responsible in forming emulsion membrane between oil and aqueous phase. The

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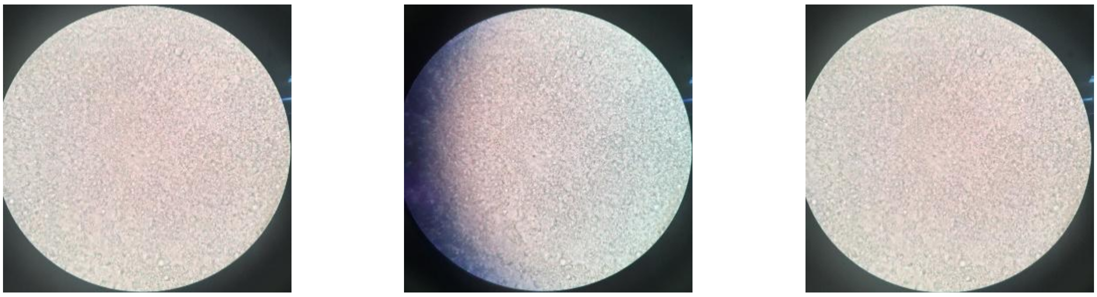
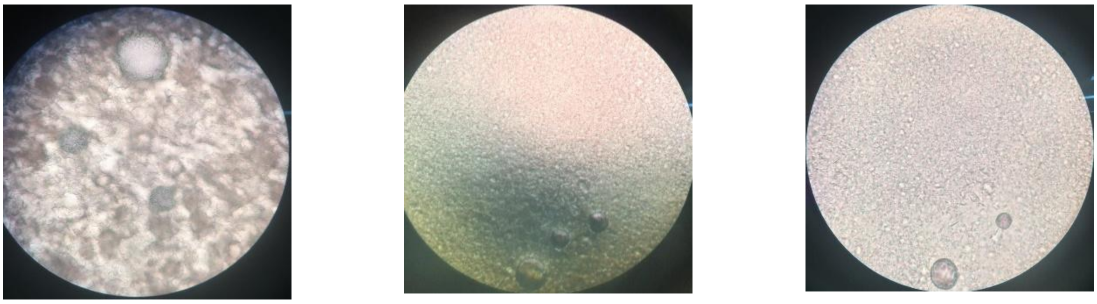
microscopic structure of the emulsions was analysed to detect any aggregation or changes in the oil droplets dispersion. Figure 1 shows microscopical view of lotion 1, lotion 2 and lotion 3 immediately after preparation. It indicates that the oil droplets are all almost uniform in size and homogenously distributed in the medium.

Physical instabilities such as flocculation, creaming, coalescence and breaking are the factors of phase separation in emulsions. Figure 2(a) is an example of a coalescence, where droplets aggregate and eventually lead to complete breaking of the emulsion formulation. Further investigation found out that Lotion 1 has some fungal growth which is later explained in this discussion. Figures 2(b) and 2(c) show the presence several droplets, an indication of an early stage of coalescence. The difference between lotion 2 and 3 is that the ratio of palm olein and coconut oil. However, the major consistency of oil droplets in these two lotions suggesting that the emulsions remain stable after six months storage.



(a) (b) (c)

Figure 1. Microscopical view after preparation of (a) lotion1, (b) lotion 2, (c) lotion 3



(a) (b) (c)

Figure 2. Microscopical view after 6 months of (a) lotion1, (b) lotion 2, (c) lotion 3

Table 3. pH and classification of sample lotions.

Samples	pH after six-month storage	Classification
Lotion 1	8.3	Basic
Lotion 2	8.7	Basic
Lotion 3	8.4	Basic
Commercial 1	4.7	Acidic
Commercial 2	3.4	Acidic

RSDL is alkaline with a pH range of 10.35 to 10.85 [20] whereas the prepared lotions were found to be in the range of 8-9 and does change significantly during the six month storage (Table 3). Their basicity is probably due to the addition of sodium hydroxide during the preparation, which raises the pH of the lotions, making them suitable to be used as reactive skin decontamination lotions [20-21]. Sodium hydroxide is a common pH adjuster in the preparation of emulsions, as well as to enhance the emulsion stability [22]. In general, commercial lotions that contain pH adjustment compound such as alkaline agents, will be basic. The pH of these lotions that were maintained over the course of six months denotes that the emulsions are at equilibrium, i.e., there is no significant change of their compositions. The pH decrease signifies an incomplete hydrolysis reaction of the oil catalysed by sodium hydroxide during emulsification. However, adding of active ingredients may slightly change on the lotion's pH which will be determined in the future work.

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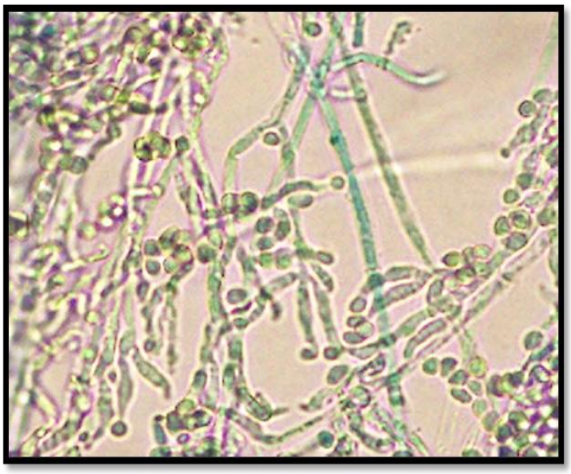

Figure 3. Microscopical analysis of the fungal present in Lotion 1

In order to be a matrix for a decontamination tool, the shelf-life of the product is important to ensure the product is stable over a storage time. Preservatives are necessary to add in the formulation as well to prevent the bacterial and fungal growth in lotions. Liquid Germall Plus is used with concentration of less than 5% in the formulation of lotion 2 and 3. It is only suitable for emulsion with the pH range of 5 to 8 as it will react to base. On the third month, lotion 1 is observed to have dark spots, suggests the presence of microbial growth. The lotion was then taken for a microscopical analysis to determine the type of contaminants. The dark spot was later analysed to be one of a fungus (Figure 3), Trichoderma *sp*. This type of fungus is widely distributed in soil, plant material, decaying vegetation and woods. This corresponds to the fact that one of the main ingredients in the prepared lotions is palm olein.

All three of the prepared lotions and selected commercial lotions were analysed using ATR-FTIR spectroscopy (Figure 4). Table 4 summarizes the main functional groups of the prepared lotions. They have very similar peaks fitting that they composed of the same compositions with vary oil to water ratio. The broad peak at 3358 cm^{-1} in the prepared lotions indicates the presence of OH stretching. This peak is characteristic of hydroxyl (OH) groups, commonly associated with water which is consistent with the high-water content (70% w/v) of the prepared lotion. Other significant peaks include peaks at 2919.80 cm^{-1} stands for C=CH stretching, 2852.57 cm^{-1} which due to and 1638.46 cm^{-1} suggests the presence of C=O triglyceride esters. The FTIR spectra of the prepared lotions were similar to the peaks mentioned in the literature [23].

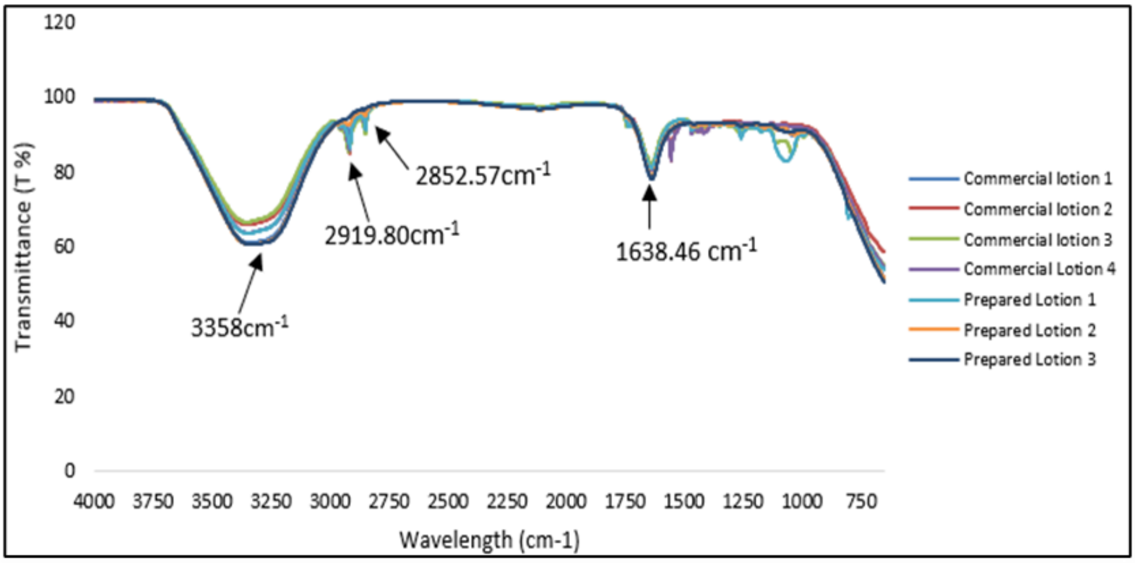

Figure 4. FTIR spectra of commercial and prepared lotions

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Table 4. Functional groups found in the prepared emulsions

Frequency (cm^{-1})	Functional group
3357.84	O-H stretching
2919.80	C=CH
2852.32	Bending vibrations of CH_2 and CH_3
1744.81	Bending vibration of CH_2 group
1644.69	C=O triglyceride esters
1464.51	CH_2
1158.66	C-O stretching
1044.52	O-CH_2 stretching

4.0 CONCLUSION

Emulsion is a promising matrix to be incorporated with active ingredients to decontaminate OPs from the contaminated skin. An increase in the utilization of organophosphate substances in terms of agriculture and chemical warfare results in increase of research studying the development of decontamination tools which refer to a variety of products and technologies designed to remove or neutralize hazardous substances [24]. From previous studies conducted, it is proven that RSDL is better than other existing decontaminants such as solid adsorbents and M-291 SDK due to its effectiveness against a wide range of chemical agents [8]. Remarkably, this work contributes to rationalize the design of topical emulsions and compared to commercial lotions. There are several components that play an important role to ensure the stability of emulsion. We discussed how the variation of the main ingredients such as the oil-water ratio or the use of different emulsifiers may affect the characteristics of emulsion. It is concluded that the prepared lotions exhibited similar functional groups when compared with the commercial lotions. The formulation of lotion 3 showed the most optimum formulation based on its pH, physical characteristics and microscopic view over a period. To reinforce skin decontamination against organophosphate substances, the best formulated lotion will then be further developed to be one of the decontamination tools.

5.0 CONFLICT OF INTEREST

The manuscript should provide full disclosure of any financial or non-financial interests, including political, personal, or professional affiliations, that could be perceived as having impacted its content. If there is no conflict of interest, the line "The authors declare no conflicts of interest" should be included.

6.0 AUTHORS CONTRIBUTION

Authors are advised to submit an author statement file that outlines their individual contributions to the paper using the relevant author contribution roles in order to enhance transparency. The primary author bears the responsibility of ensuring that other authors are in agreement regarding the accuracy of the descriptions. It is necessary to specify the duties of all authors, using the suitable categories below. Authors may have fulfilled a diverse range of roles in their contributions. Author contributions do not influence the criteria for authorship set by the publication. The subsequent terms are employed to characterise author contributions.

Conceptualisation; Methodology; Validation; Formal analysis; Data curation; Formal analysis; Investigation; Resources; Software; Visualisation; Writing - original draft; Writing - review & editing; Funding acquisition; Project administration; Supervision.

Authorship statements should be presented with the authors' names listed first, followed by their respective author contribution role(s), such as

First, J. A. (Conceptualization; Methodology; Formal analysis)
Second, J. A. (Resources; Software; Data curation; Writing - original draft; Resources)
Third, J. A. (Writing - original draft; Project administration; Supervision)

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