Palm olein solid soap as a matrix for organophosphate decontamination agents

N S Abdul Latif 1, H Ariff2, R A Mohamed1,3, N Abdul Halim4, S A Mohamad Noor3,4 O K Khim3,4, N A Mohd Kasim3,4, and W M Z Wan Yunus1,2

1 Centre for Tropicalisation, National Defence University of Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur
2 Faculty of Defence Science and Technology, National Defence University of Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur
3 Research Centre for Chemical Defence, National Defence University of Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur
4 Centre for Defence Foundation Studies, National Defence University of Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur

*Corresponding author: wanmdzin@upnm.edu.my, shazwani@upnm.edu.my

Abstract. Penetration of organophosphates through skin is one of the major routes for organophosphate poisonings which are associated with acute injuries and deaths. Thus, immediate and effective decontamination of these chemicals from the exposed skin is essential to prevent them from entering the body. Soap solutions which have a capacity to remove effectively the organophosphates from the skin, can be modified by adding suitable additives, to make them capable to convert the poisons into harmful chemicals to the environment. Although soaps are commercially abundant, their exact formulations are unknown. In order to understand soap interactions with their additives, the knowledge of the soap compositions is needed. In this paper, we describe the results of our attempts to synthesise soaps from palm olein and coconut oil by saponification process using sodium hydroxide. Our study showed that, the soap synthesized from palm olein and sodium hydroxide solution has similar physicochemical properties with those of the selected commercial soap. This soap will be modified and further characterised for removal of organophosphates from contaminated skins. This paper report results of our preliminary study on the soap characterization prior to formulation of the soap with active ingredient as organophosphate decontamination agent.

1. Introduction
In the agricultural industry, organophosphates (OPs) are among the most commonly used pesticides worldwide. According to a report on Pesticides Industry Sales and Usage Estimates 2008-2012, the total amount of pesticide usage globally was around 2.7 billion kilograms annually in both 2011 and 2012 [1]. The objective of using OPs in the agriculture industry is to reduce crop losses, however it can lead to the poisoning of the environment since the chemicals are toxic compounds which also become a major threat to humans who synthesize and use them. In addition, these chemicals have been abused as neurotoxins since World War II [2]. At its worst, OPs have been synthesized in a large scale and used as chemical nerve agents during military crisis and in terrorist attacks [3]. This abused is continued till
today with the recent incident was the use of OPs in Syria civil war. The mechanism of action of these nerve agents is through inhibition of acetylcholinesterase (AChE), an enzyme that involved in the transmission of nerve impulses. The inhibition of this enzyme leads to acetylcholine accumulation which among its effects includes severe functional disturbances at respiratory, cardiovascular, muscular, pupillary, and digestive system, and can be worsen to ultimately lead to death [4].

Accidental pesticide poisoning resulting from OP exposures are major cause of deaths. Upon exposure, these chemicals penetrate into the body via the percutaneous pathway. Therefore, in managing a patient exposed to OPs, the initial step is to decontaminate the patient to stop the compounds from further entering the body[5]. The decontamination is a phase of eliminating or/and neutralizing the harmful substances from the personnel, equipment as well as environment. An effective decontamination process must be performed within the first few minutes after the exposure. Historically the first decontaminants that were employed for removing chemical nerve agents were bleaching powders such as calcium hypochlorite or sodium hypochlorite. However, these chemicals may not be suitable for use in decontaminating the skin as they are moderately toxic and could produce temporary side effects such as redness, skin irritation and allergic reaction. Ideally, the decontamination agent used should be non-corrosive, easy to apply, have low toxicity, and remain stable for length of time after its preparation [6].

During incidents where there is OPs contact, the standard decontamination procedure used is to wash away the chemicals, but this method demonstrates a serious drawback as the contaminants are only removed and diluted, but not fully neutralized or destroyed[4]. The surrounding area of the decontamination shower site may be affected by the effluent from the decontamination shower and then contaminate other areas if the decontamination effluent is not carefully managed and disposed. Use of a soap that can deactivate and degrade the OPs will be an effective solution to this problem. Therefore, this study is aimed to synthesis a solid that can be used for this purpose. In fact, in the literature there are very limited studies pertaining to the usage of soap with active ingredient as matrix for organophosphate decontamination agent. Perhaps, a soap prepared from plant based products, with no colorant and preservatives, non-toxic and environmentally- friendly would be a preferable choice compared to contemporary commercial soaps that contain synthetic chemicals such as triclosan and chloroxylenol, some of which may carcinogenic and can cause allergic responses [7].

Soap is a product of a saponification reaction between fatty acids or tryglycerides and an alkali solution such as sodium or potassium hydroxide. Many soap formulations are based on petrochemicals or/and animal fats. To cater for halal market demands, plant- based oils such as palm, coconut and olive oil are used for soap production. Malaysia as one of the largest palm oil producer globally has great availability of this raw material for the soap making process. Moreover, an advantage of palm oil is it improves the hardness of solid soap and creates lather when paired with coconut oil. In fact, hardness, cleansing power and lathering properties are some of the values that determines the quality of soap [8]. Thus, this present study is aimed at producing solid formulations using different weight ratios of palm olein and virgin coconut oil blend to obtain a suitable product for the effective and safe removal of OP compounds from contaminated skins.

1. 2. Materials and Methods

2.1 Oils
Virgin coconut oil was purchased from a local retailer in Kuala Lumpur, Malaysia while palm oil was a gift from Sime Darby Research Sdn. Bhd.

2.2 Solvents and reagents
For the synthesis of soap, the sodium hydroxide used was analytical grade. Sample of two commercial bar soaps were purchased from a local store in Kuala Lumpur, Malaysia.

2.3 Preparation of soap
Saponification process was carried out using six chosen palm olein and virgin coconut oil blends. The oil blends were first heated to 80°C and then followed by adding the lye solution into them. The mixtures were then stirred for 10 minutes to obtain a thick, creamy and smooth traces, poured into a mould and left to set for 24 hours at room temperature. The details of the six soap formulations are given in Table 1.

| Sample | PC1 | PC2 | PC3 | PC4 | PC5 | PC6 |
|--------|-----|-----|-----|-----|-----|-----|
| Palm olein: virgin coconut oil blending ratio (g/g) | 100:0 | 80:20 | 60:40 | 40:60 | 20:80 | 0:100 |
| Sodium hydroxide (g) | 12.0657 | 12.0660 | 12.0908 | 12.0829 | 12.0040 | 12.0428 |
| Deionised water (g) | 30.1460 | 30.0574 | 30.2282 | 30.1791 | 30.5087 | 30.0220 |

2.4 Characterisation of soaps
All the prepared soaps were characterised by their FTIR spectra, colour, pH, foaming ability, hardness, and effectiveness in cleaning.

2.4.1 FTIR Spectrometry. Fourier transform infrared analysis (FTIR) spectrometry of oil and soap samples were performed using Perkin Elmer Spectrum IR 10.6.1. The FTIR spectra were recorded from 4000 to 650 cm\(^{-1}\). The software used for FTIR data collection was Spectrum IR version 10.6.1. Prior to analysis, the ATR plate was cleaned by scrubbing with acetone using soft tissue paper [9]. The plate cleanliness was verified by running a background spectrum. Next, the soap samples were placed on the clean ATR plate and spectra result was recorded as absorbance values indicated.

2.4.2 Colour Analysis. All prepared soap samples were hardened after 24 hours of preparation. The color changes of the soaps vary differently according to the blend ratio of palm olein and virgin coconut oil. The colour analysis were observed by direct vision.

2.4.3 pH Analysis. Measurement of the pH values of the soap solution was carried out using a pH meter (Hanna HI 8424). The solution was prepared by dissolving one gram of the soap sample in 100.00 ml deionised water [8]. The pH was recorded after the electrode in the soap solution gave the stable reading.

2.4.4 Foaming Ability. Two grams of each solid soap sample was dissolved in 50.00 ml of deionised water in a 100.00 ml measuring cylinder. The solution was shaken vigorously for 2 minutes and left standing for 10 minutes [7]. The foam height was then measured (cm).

2.4.5 Hardness Test. To determine the hardness of the soaps, a needle (3.5 cm long; diameter 1.0 mm) was loaded with a fishing weight (103.58 g) and gently vertically placed with the sharp point of the needle touching the surface of the soap. The distance at which the needle penetrated the soap after 5 seconds was recorded as a measure of its hardness [7]. The hardness test was carried out three times for each sample of soap and mean penetration was reported.

2.4.6 Effectiveness of Cleaning. To determine the soap cleaning effectiveness, a filter paper strip of size 5.0 cm by 1.0 cm which was stained with a drop of oil-based dye was soaked in 100.00 ml of 2% (w/v) soap solution in a 100.00 ml measuring cylinder. The measuring cylinder was shaken up and down vigorously using hand for one minute. The filter papers were then removed from the measuring cylinder and rinsed. The degree of cleanliness in each filter papers were observed and recorded as totally removed, moderately removed, poorly removed or not removed [10].
3. Result and discussion

3.1 FTIR spectrometry.
Figure 1 and Figure 2 show the palm olein and virgin coconut oil spectra and their important functional groups shown in the spectra are given in Table 2 and Table 3, respectively.

![FTIR spectrum of palm olein](image)

**Figure 1.** FTIR spectrum of palm olein

| Frequency (cm\(^{-1}\)) | Functional group assignment                                      |
|-------------------------|------------------------------------------------------------------|
| 2922 and 2853           | Asymmetrical and symmetrical stretching vibration of methylene (-CH\(_2\)) group |
| 1744                    | Ester carbonyl functional group of triglycerides                  |
| 1465                    | Bending vibrations of CH\(_2\) and CH\(_3\) aliphatic groups      |
| 1377                    | Bending vibration of CH\(_2\) groups                             |
| 1160                    | C-O stretching                                                   |
| 1116                    | Stretching vibration of the C-O ester group                      |
| 721                     | Overlapping of methylene (-CH\(_2\)) rocking vibration           |
Figure 2. FTIR spectra groups of virgin coconut oil

Table 3. Functional groups identified in virgin coconut oil

| Frequency (cm\(^{-1}\)) | Functional group assignment                        |
|-------------------------|---------------------------------------------------|
| 2922 and 2853           | C-H stretching vibration                          |
| 1743                    | Ester carbonyl functional group of triglycerides  |
| 1465                    | Bending vibrations of CH\(_2\) and CH\(_3\) aliphatic groups |
| 1377                    | Bending vibration of CH\(_2\) groups              |
| 1154                    | C-O stretching                                    |
| 1110                    | Stretching vibration of the C-O-C and C-H bending |
| 721                     | Overlapping of methylene (-CH\(_2\)) rocking vibration |

The FTIR spectra of the palm olein and virgin coconut oil used in the preparation of soaps were similar to that found in FTIR results published in the literature [9].

The FTIR spectra of PC 1, PC 2, PC 3, PC 4, PC 5 and PC 6 show that they are similar products as of the Commercial 1 and Commercial 2 soap.
3.2 Soap Colour

The colour of the soap prepared from 100% palm olein was yellow. However, the intensity of the yellow colour decreased as the percentage of the virgin coconut oil content was increased. This is expected as the soap prepared from 100% virgin coconut oil was white in colour. All the prepared soap was solidified well after 24 hours. When compared to the Commercial 1 and Commercial 2, these commercial soaps were much harder compared to that of the prepared soaps. This may be due to the synthesised soap samples were not fully cured.

**Figure 3.** FTIR spectra of PC 1, PC 2, PC 3, PC 4, PC 5, PC 6, Commercial 1 and Commercial 2 respectively.
Table 4. Physical properties of soaps prepared from various palm olein and virgin coconut oil blends.

| Sample of soaps | Palm olein: virgin coconut oil blending ratio | Colour       | Physical Texture | Picture |
|-----------------|---------------------------------------------|--------------|------------------|---------|
| PC 1            | 100:0                                       | Creamy Yellow | Hard             |         |
| PC 2            | 80:20                                       | Creamy Yellow | Hard             |         |
| PC 3            | 60:40                                       | Creamy Yellow | Hard             |         |
| PC 4            | 40:60                                       | Light Yellow  | Hard             |         |
| PC 5            | 20:80                                       | Light Yellow  | Hard             |         |
| PC 6            | 0:100                                       | White         | Hard             |         |
| Commercial 1    | -                                           | Yellow        | Very Hard        | -       |
| Commercial 2    | -                                           | white         | Very Hard        | -       |

3.3 Soap pH
Figure 4 showed the pHs of the prepared and two commercial soaps. The pHs of PC3 to PC6 soap samples were within the range of 7 to 10 which correspond to the recommended range of pH for normal soap which is 8-10 [11]. The pH for PC 1 of 10.31 is similar to the palm olein soap described by [12] which was pH 10 as well as the Commercial 1 soap. The high soap pH is probably due to incomplete usage of sodium hydroxide during saponification. The high alkalinity can be overcome by adding an excess of the calculated oil substrate or by using superfatting agents [10]. The superfatting agents can be used from distilled fatty acids including lauric, myristic, stearic and palmitic acids [13].
3.4 Hardness test

Figure 5 illustrates the hardness test results of the soap samples which were tested by measuring the level of penetration of the needle into the soap. The harder of a soap, the higher its ability to slowly dissolve in water, thus making it last longer [8]. From the results obtained, soap PC 1 was harder compared to other soap samples with 0.9 cm needle penetration, while both commercial soaps showed only 0.4 cm and 0.36 cm penetration respectively in which they were the hardest among the tested samples. Based on these results, soap samples prepared from palm olein solely (PC 1) was harder compared to the other prepared soaps. As the soap samples were coconut oil blended, the degree of hardness was reduced significantly.
3.5 Foaming test
Figure 6 shows the ability of soaps to form foam. Based on the foaming ability test carried out on the eight samples of soap, Commercial 1 soap exhibited the highest foamability with the foam height of 15.0 cm. The result for the prepared soaps ranged from 9.3 to 14.4 cm which are lower than those of the commercial soaps.

![Figure 6. Result of the foaming ability test of the six prepared and two commercial soaps.](image)

3.6 Effectiveness of cleaning
Palm oil contains 40-52% oleic, 32-47% palmitic, 5-11% of linoleic, and 2-8% stearic acids. Fatty acids such as oleic, palmitic, lauric and stearic are responsible for the cleansing action of soap [14] and they also produced stable lather. From the soap samples cleaning tests, it was found that PC 1, PC 2 and Commercial 1 soap can clean very well. However, the cleaning effectiveness were moderate for PC 4, PC 5 and PC 6 and was very poor for PC 3 and Commercial 2 soap. This very poor effectiveness was probably due to the pH value of that soap. Efficiency of washing depends on the concentration of hydrogen ions in the soap solution whereby maximum effectiveness is attained when pH solution is 10.7 [15]. Hence the formulations of soap with a higher ratio of palm olein is desirable to retain the best cleaning effects.

4. Conclusion
Bar soaps were successfully prepared from palm and virgin coconut oils through saponification process. FTIR spectra, pH, foamability and cleaning effectiveness studies showed that can be used as a base for synthesising an organophosphate removal decontaminant. However, further investigation is needed for incorporation of additive to obtain organophosphate removal capability.

5. Acknowledgements
The authors would like to thank the National Defence University of Malaysia (NDUM) for providing research facilities, the Ministry of Education Malaysia and The Government of Malaysia for the research grant and the Sime Darby Research Sdn. Bhd. For providing palm olein sample.
References

[1] Atwood D and Paisley-Jones C 2017 Pesticides industry sales and usage 2008-2012 Market Estimate Biological and Economic Analysis Division Office of Pesticide Programs p 24
[2] Ghorab M A 2015 Toxicological effects of organophosphates pesticides Int. J. Environ. Monit. Anal. 3 218
[3] Worek F and Thiemann H 2013 The value of novel oximes for treatment of poisoning by organophosphorus compounds Pharmacol. Ther. 139 249–59
[4] Salerno A, Bolzinger M-A, Rolland P, Chevalier Y, Josse D and Briancon S 2016 Pickering emulsions for skin decontamination Toxicol. Vitr. 34 45–54
[5] Salerno A, Devers T, Bolzinger M-A, Pelletier J, Josse D and Briancon S 2017 In vitro skin decontamination of the organophosphorus pesticide paraoxon with nanometric cerium oxide CeO2 Chem. Biol. Interact. 267 57–66
[6] Gordon R K and Clarkson E D 2009 Rapid decontamination of chemical warfare agents Handbook of Toxicology of Chemical Warfare Agents (Academic Press) chapter 71 pp1069-81
[7] Ameh A O, Muhammad J A and Audu H G 2013 Synthesis and characterization of antiseptic soap from neem oil and shea butter oil African J. Biotechnol. 12 4656–62
[8] Atolani O, Olabiyi E T, Issa A A, Azeez H T, Onoja E G, Ibrahim S O, Zubair M F, Oguntoye O S and Olatunji G A 2016 Green synthesis and characterisation of natural antiseptic soaps from the oils of underutilised tropical seed Sustain. Chem. Pharm. 4 32–9
[9] Rohman A 2016 Infrared spectroscopy for quantitative analysis and oil parameters of olive oil and virgin coconut oil: A review Int. J. of Food Prop. 20 1447-56
[10] Warra A A, Hassan L G, Gunu S Y and Jega S A 2010 Cold process synthesis and properties of soaps prepared from different triacylglycerol sources Niger. J. Basic Appl. Sci. 18 315–21
[11] Mak-Mensah E E and Firempong C K 2011 Chemical characteristics of toilet soap prepared from neem (Azadirachta indica A. Juss) seed oil Asian J. of Plant Sci. and Res. 1 1-7
[12] Oluwatoyin S M 2011 Quality of soaps using different oil blends J. Microbiol. Biotechnol. Res. 1 29–34
[13] Benjamin S E and Abbass A 2019 Effect of superfatting agents on soaps properties J. Oil Palm Res. 31 304–14
[14] Shahinuzzaman M, Yaakob Z and Moniruzzaman M 2016 Medicinal and cosmetics soap production from Jatropha oil J. Cosmet. Dermatol. 15 185–93
[15] Rhodes F H and Bascom C H 1931 Effect of pH upon the detergent action of soap Ind. Eng. Chem. 23 778–80