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Decontamination of Organophosphates: Efficacy of Oxime Incorporated Palm Oil based Liquid Soaps for Methyl Parathion Neutralization

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ABSTRACT

Organophosphates (OPs) are a group of poisonous chemicals that are commonly used as pesticides and at times as chemical weapons. Decontamination of these compounds from the contaminated surfaces is an important step in their poisoning incident management but techniques that are commonly used currently, washings with soap solutions are not effective as the contaminants are still active in the waste solutions. Addition of an active ingredient such as an oxime which acts as a nucleophile in the soap solutions will enhance the ability of the washing liquids to hydrolyse OPs to convert them into innocuous compounds. This article describes a procedure to synthesize and characterize oxime-incorporated palm oil-based liquid soaps with an oxime concentration in the range of 0.05–1% and the results of their evaluation for their decontamination efficacy to degrade the OPs into non-toxic compounds. The soaps were formulated from palm oil and stable with the pH of 11.0, which is within the pH range for decontamination purposes. Upon mixing the soap solutions with Methyl Parathion (MP), the MP degrades slowly with the formation of p-nitrophenol (p-NP) after 24h which appears at peaks 400nm of the UV-Visible spectrum. However, in the presence of 2-pyridine aldoxime methiodide (2-PAM) with concentrations of 0.05% to 1.0%, the degradation is immediately observed involving the 2-PAM/MP complexation, in addition to the formation of p-NP after 24h. Furthermore, with the concentration of 2-PAM of 0.5% to 1.0%, the degradation does not produce p-NP but dimethylthiophosphate (DMPT) suggesting that the oxime content in the soap is sufficient to neutralise the MP. Based on the above findings, it can be concluded that the addition of the 2-PAM at the right concentration into the soaps significantly enhances their ability to efficiently decontaminate MP.

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1. Introduction

Organophosphorus compounds are organic compounds containing trivalent or pentavalent phosphorus and generically often referred to as organophosphates (OPs) [1]. Figure 1 illustrates the general formula of OPs which contains a central phosphorous atom connected to a terminal oxygen or sulphur atom by a double bond, as well as two lipophilic groups (R1 and R2) attached either directly to the central atom (phosphinates) or via sulphur (phosphothoiates) and oxygen atoms (phosphothoiates) (phosphates). An additional X group, which may be aliphatic, aromatic, or heterocyclic, binds to phosphorus via an oxygen or sulphur atom [2].

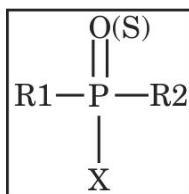


Fig. 1. Generic Structure of OPs

Organophosphates (OPs), which are normally the esters of phosphoric acid (P=O) and thiophosphoric acid (P=S), were used as flame retardants, insecticides and parasiticides in veterinary medicine but majority of these compounds are used as pesticide for crop yield enhancement due to their low environmental stability but high insecticidal toxicity [3,4]. Various pesticides are used in today to eliminate unwanted organisms during the planting process. It is well documented that the use of pesticides has increased the quality and quantity of agricultural products [5].

Over the past forty years, around 100 different OPs have been developed and commercially available in the market. Hexaethyltetraphosphate (HETP) was the first OPs created, which was well-known for its insecticidal properties in agricultural settings. Then, several additional OPs compound, such as Parathion, Paraoxon, Malathion, Monocrotophos, Coumaphos, and Chloropyrifos, etc., were explored [6]. Unfortunately, these pesticides pose a variety of risks to environment and organisms, including people, and inhibit microbial activity in soil, making the use of this chemical a source of concern [7].

In addition, despite the advantages of pesticides in agriculture, these OPs can also be further developed into chemical warfare agents (CWAs) as the products are highly toxic compounds [8]. This led to the discoveries of Tabun by Gerhard Schrader in 1937 and later of more other deadliest toxic agents. CWAs can be categorized into four groups (Figure 2) comprises of Sarin (GB), Soman (GD), and Cyclosarin (GF) that are categorised as Group I chemicals while V series compounds (such as VX and VR) are in Group II. Tabun (GA) and a GV compound are example of OPs in Group III and IV, respectively [9]. These compounds are very dangerous because they can be rapidly absorbed through the skin and have been used since World War II against both the military and civilians [10].

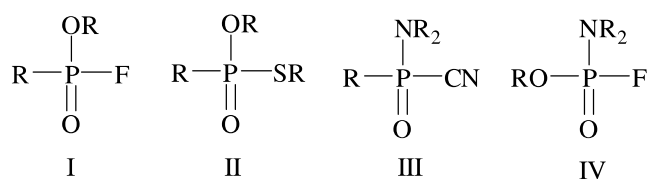


Fig. 2. Groups of OPs

The most dangerous and deadly pollutants, known to have catastrophic effects on both humans and the environment, are chemical warfare agents [11]. Methyl parathion (O, O-dimethyl O-4-nitrophenyl phosphorothioate, MP) is an important organophosphate pesticide, and can be used as a simulant for CWA especially V-type (Group II) nerve agents and poses a serious threat worldwide, although it has been banned in many countries due to unnecessary stockpiling and prohibited misuse of this agents (common to many OPs and OTPs) [12,13]. In the early 1950s, MP was widely employed as an agricultural pesticide after its introduction to the market [14]. However, due to its severe toxicity even at low dosage and persistence in the environment, World Health Organization (WHO) has classified MP as an extremely hazardous insecticide (Class I) [15]. In February 2017, a member of the Kim family was assassinated in Malaysia by applying a binary form of VX agents to the victim's face and eyes [16].

The greatest concern regarding these types of OPs is that their high mortality, even at a trace level of exposure [17]. Therefore, there is a concerted global effort to prevent the use and development of chemical agents due to the increasing usage of these substances. Despite these efforts made incidents that involve the use of these chemical agents are still become a major threat of death, injury, and destruction [18].

The widespread uses and high permeability through ingestion, inhalation, and skin exposure contribute to a significant number of recorded cases of OPs poisoning [19]. The main mechanism of OPs toxicity was by inhibiting acetylcholinesterase (AChE) enzyme activity which plays a crucial role in breaking down or hydrolyzes acetylcholine (ACh), a naturally occurring neurotransmitter, into acetic acid and choline which primarily found at postsynaptic neuromuscular junctions [20,21]. Acetylcholinesterase (AChE) inhibitors, such as OPs neurotoxins and their chemically related insecticides, can inhibit AChE and cause a cholinergic crisis which ultimately cause death [22].

Both OP-based insecticides and OP-based nerve agents have the same mechanism of action to cause OPs poisonings. Chemical weapons that use nerve agents, which are OP compound derivatives, are particularly hazardous. In addition, pesticide uses, and several chemical agents built on OP compounds have been misused in recent years and pose a lethal threat to the environment and mankind [23]. OPs are a leading cause of poisoning worldwide, killing over 100,000 people annually because of their extensive use in agriculture and the high risk of accidental or intentional exposure [24].

Thus, their persistence in the environment and the potential for acute and chronic toxic effects on humans and ecosystems necessitate effective decontamination strategies. Decontamination is an important step in managing incidents of organophosphate poisonings. It is a process of removing the agents from people, equipment, and premises that have been exposed to these chemicals, and, therefore, by their effective removal, both the victims and first responders such as healthcare workers can be protected [25]. Decontaminations are classified as either mechanical, physical, or chemical methods. The first chemical decontaminant that was used against CWAs was a bleaching powder, such as calcium or sodium hypochlorites. Although the ability of these chemicals to remove the CWAs was encouraging, their lack of stability limits their usages [26].

The standard decontamination procedure that involves using a shower to remove the agent from the skin, may cause systemic exposure due to the "wash-in effect" of using of abundance showering water [27]. Furthermore, since not all chemicals are degraded or neutralised, the showering procedure may lead to a major drawback [28]. The current systems for effective decontamination used by military or civilians after incidents of chemical attacks include removal by Fuller's Earth (FE), Reactive Skin Decontamination Lotion (RSDL), M291 Decontamination Kit, and IPB-80 Decontamination Kit [29-32]. Despite various decontamination systems being used, decontamination procedure by washing with soap or surfactant and water is still widely used [33].

OPs can be degraded through chemical decontamination [34]. Current research trends in chemical decontamination or degradation include the use of chelates and nanocrystalline metal oxides as photocatalytic degradation, the use of the use of metal-organic frameworks (MOFs) and polyoxometalates (POMs) to catalysing the rapid hydrolysis process, the development of functionalized bead cellulose, effective sorbents for removal of pesticides, organic and inorganic contaminants and the degradation of OPs using pyridinium-based functional surfactants [11,35-44].

Over recent years, the demand for liquid soap or surfactant has been increasing because it is much easier for everyday use and has a performance cleaning effect [45]. The potential of using a palm oil-based liquid soap in decontamination is great, especially in the context of it being a plant-based natural ingredient and having good biodegradability as well as Malaysia's status as one of the top producers of palm oil and its convenient access to all essential raw materials [46].

It has been shown that oximes can be used to create functionalized structured molecular systems. 2-Pyridine aldoxime methiodide (2-PAM), an oxime, is known to be the crucial antidote for organophosphate poisonings as they can react as acetylcholinesterase reactivators [47]. It also can act as a nucleophile (Nu-) that enhances the hydrolysis of OPs by creating efficient functionalized surfactants with high nucleophilicity and solubilizing power. Functionalized surfactants belong to the class of most potent reactants in their ability to cleave P-O bond in OP esters [2].

This report describes the results of our work to produce a more effective soap based washing reagent for decontaminating of OPs from contaminated surfaces. The reagent is prepared by incorporating 2-PAM in a liquid soap synthesised from palm oil by a saponification process using KOH. Addition of this oxime compound into this soap solution improves drastically the time of the soap to degrade the contaminant as monitored using UV-Vis and FTIR Spectrophotometry [48].

2. Methodology

2.1 Preparation of Oxime Incorporated Oil Palm Based Liquid Soaps

The palm oil liquid soap was prepared by a saponification process. The palm oil (0.005 mol) was first transferred into a beaker and stirred at a temperature of 80 °C. This was followed by the addition of 0.03 mol of potassium hydroxide (KOH) which was dissolved in 50ml ultra-pure water into the beaker. The mixture was continuously stirred at 200 rpm and heated for about 6 hours until homogeneous traces of soap were formed. The soap formed was then weighed and transferred into a bottle, diluted with ultra-pure water in a ratio of 1:5 (v/v) and stirred until they became homogenous and left for 24 hours. To obtain 2-PAM incorporated soap of the 2-PAM concentrations ranging from 0.05% to 1% w/v, the required amount of the oxime was added and stirred for 5 minutes. The homogenous liquid soap obtained was then stored in an air-conditioned room at 20 °C.

2.2 Physicochemical Properties Evaluation of Oxime Incorporated Oil Palm Based Liquid Soaps

The liquid soaps which were stored for two weeks were used for the physicochemical and chemical stability evaluations. Their color appearance, stability, foamability stability and pH were studied as follows:

2.2.1 Stability study

Centrifugation and mechanical vibration test were performed on the liquid soap to determine the stability. Two mL of the soap solution was transferred into Eppendorf tubes and centrifuged at 5500 rpm for 15 minutes using MultiFUGE Mini-Centrifuge (Clever Scientific Ltd.). Meanwhile, for

mechanical vibration test, 5 mL of each liquid soap formulations were placed in an Eppendorf tube and subjected to vibration on a vortex shaker for 10 seconds.

2.2.2 Foamability study

Foamability study was carried out based on the procedure described by previous study with slight modification [49]. The foam was first generated by vigorously shaking 10 mL of liquid soap solution in a closed 50-mL Eppendorf tube on a vortex shaker. The shaking with the same intensity was carried out for ten times for each test sample, and the foam height above the liquid level in the tube was determined over a period of 60 minutes for foam stability.

2.2.3 Determination of pH

The pHs of liquid soap solutions were determined using a calibrated pH meter (Mettler Toledo Benchtop pH Meter). The samples for the pH measurement were 10% of the liquid soap solutions which were prepared by diluting the original soap solutions with ultra-pure water and stored in an air-conditioned room for 1 hour. Three pH readings of each sample were recorded in triplicate, and the average was recorded.

2.3 Fourier-Transform Infrared Spectroscopy

The presence of the functional groups in liquid soap formulations before and after mixing with Methyl Parathion (MP) were determined from their spectra recorded by FT-IR Spectrometer Frontier (Perkin Elmer) of from 600 to 4000 cm^{-1} with 4 cm^{-1} resolution recorded after 8 scans. A drop of a liquid soap was deposited and covered the crystal diamond area to ensure the sample could be scanned and evaluated. This procedure was adopted from the previous publication with minor modification [50].

2.4 Organophosphate Degradation Efficacy Monitoring using UV-Vis Spectrophotometry

The UV-Vis spectra were recorded in the range of wavenumber of between 200 and 500 nm using a Shimadzu UV-3600 I Plus UV-VIS-NIR Spectrophotometer to qualitatively monitor the presence of p-nitrophenol, the product of the Methyl Parathion degradation after reacting with 2-PAM and the formation of 2-PAM/MP complex [51,52]. The degradation reaction was carried out using 2 mL of liquid soap solution in an Eppendorf tube. After the reaction was initiated by adding a freshly prepared MP solution (400 μl of 30 μM), the reaction solution was then transferred into a cuvette and its spectra at reaction intervals of 0, 10, 30, 60 minutes, 24 hours and 72 hours were recorded. The analysis was continued and monitored for up to two weeks (interval 7 days) to observe the degradation process of MP.

3. Results

3.1 Physicochemical Characterization of Oxime Incorporated Oil Palm Based Liquid Soaps

The physicochemical properties of the prepared liquid soaps are shown in Table 1 and Figure 3. Without the presence of the 2-PAM the soap liquid is very pale yellow, and the intensity of this color increases as the quantity of the oxime in the soap is increased. In addition, they are stable liquid soaps as there no precipitation or color change observed under the test conditions. Furthermore,

their pH values of just over 11.00 are within the range for decontamination purposes. Previous study by Oudejans *et al.*, [53] stated that Malaoxon is rapidly hydrolyzed into byproducts at pH of higher than 11. They also reported that the pH of four decontamination products (EasyDECON® DF200, Sterilex Ultra Kleen Solution 1 and 2, Clorox® Concentrated Germicidal Bleach, and Pic and Span® Liquid Multi-Surface and Floor Cleaner) ranged from pH 9.40 to 11.40 [53].

Table 1

Physicochemical properties of the palm oil-based liquid soaps with and without 2-PAM incorporation

Label/2-PAM content	Colour Appearance	Centrifugation Test	Mechanical Vibration Test	Foam Height/cm	pH Analysis	
					1 st Week	2 nd Week
ST1/0%	Very pale yellow	No phase separation	No phase separation	2.2	11.33	11.20
ST2/0.05%	Pale yellow	No phase separation	No phase separation	2.3	11.15	11.23
ST3/0.10%	Pale yellow	No phase separation	No phase separation	2.4	11.26	11.26
ST4/0.5%	Yellow	No phase separation	No phase separation	2.7	11.21	11.33
ST5/1.0%	Dark Yellow	No phase separation	No phase separation	2.9	11.16	11.29

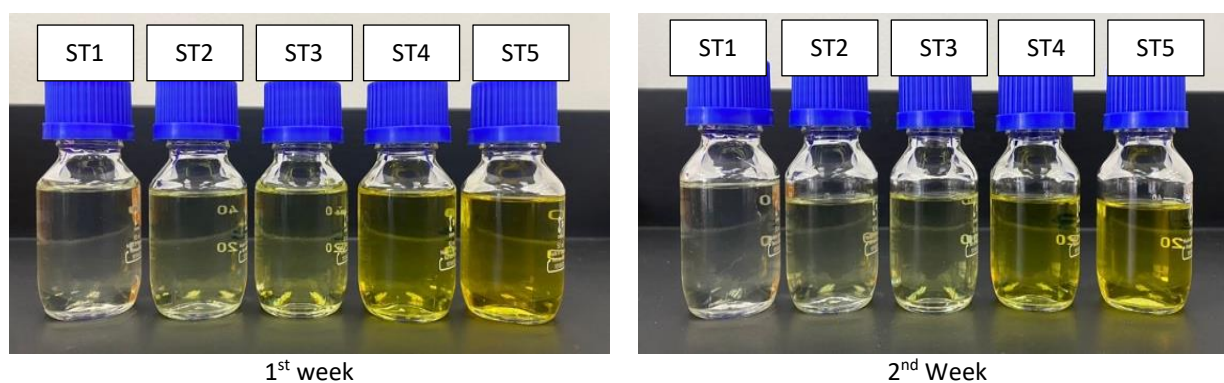


Fig. 3. The appearance the soaps with various contents of 2-PAM after one and two weeks of preparation: ST1, 0%; ST2, 0.05%; ST3, 0.1%; ST4, 0.5% and ST5, 1.0%

3.2 Characterization of Oxime Incorporated Palm Oil Based Liquid Soaps Using FTIR Analysis

The broad absorption at the peak ranging between 3000 cm^{-1} and 3500 cm^{-1} , indicates the presence of the hydroxyl group (-OH). Meanwhile, the small absorption peak of between 2800 cm^{-1} and 3000 cm^{-1} is due to the stretch vibration of the C-H bond, and the peak between 1500 cm^{-1} and 1600 cm^{-1} is for carbonyl carbon (C=O). Mirghani *et al.*, [54] described the absorption peak ranging between 1500 cm^{-1} and 1600 cm^{-1} is owing to the carbonyl carbon (C=O) group from the fatty acid-sodium salts (R-COONa).

FTIR spectra of the 2-PAM incorporated, and original palm oil liquid soaps are depicted in Figure 4(b). The absorption peak between 2968 cm^{-1} and 2842 cm^{-1} shows the presence of stretching vibration of the C-H bond. The absorption peak in $1738\text{--}1735\text{ cm}^{-1}$ indicates the existence of C=N stretching. Meanwhile, the peak at $1368\text{--}1364\text{ cm}^{-1}$ is for the occurrence of C-N stretching from aromatic amine compounds, and the $1217\text{--}1206\text{ cm}^{-1}$ is for the presence of C-O stretching from ester groups (Figure 4(b)). The presence of C=N and C-N functional groups indicates that the oxime is successfully incorporated in the soaps. Similar absorption peaks, i.e., at 3272 cm^{-1} for O-H stretching

vibration, at 2922 cm^{-1} , 2853 cm^{-1} , and 1469 cm^{-1} of asymmetric stretching of C-H and at 1665 cm^{-1} for C=N stretching vibration for an amidoxime were reported by Huang *et al.*, [55].

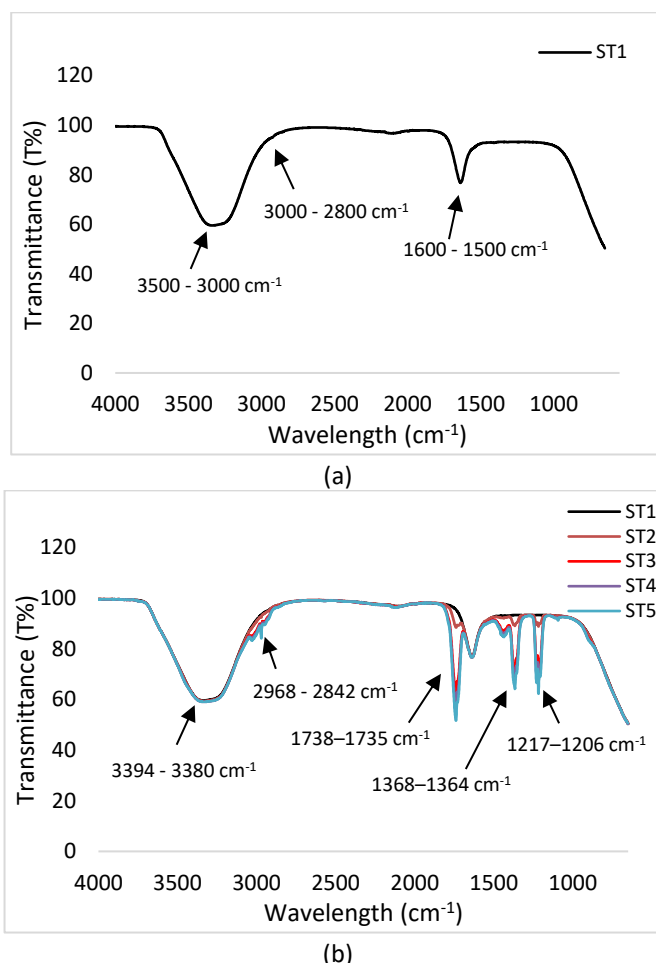


Fig. 4. (a) FTIR spectrum of palm oil liquid soap (ST1), (b) FTIR spectra of oxime incorporated and original palm oil liquid soaps of various oxime contents

3.3 Organophosphate Degradation Efficacy using FTIR Analysis

ATR-FTIR spectroscopy was used to study the interaction of MP and oxime-incorporated palm oil-based liquid soap. Figure 5(a) and Figure 5(b) show the ATR-FTIR spectra of the solutions produced after MP was added into the oxime soap solutions after 24 hours and 7 days, respectively. The existence of prominent peaks between 2900 cm^{-1} and 2800 cm^{-1} (peak 1), and 1700 cm^{-1} and 1100 cm^{-1} (peaks 2 to 7) are due to the by-products formation from the reaction of 2-PAM and MP. These results were also supported by previous study, which found an observed absorption band of 1800 cm^{-1} and 1000 cm^{-1} to in the goethite system, which indicate the formation of chemical bonds between the catabolic intermediates of MP [49].

The occurrence of absorption peaks at 1738 cm^{-1} (peak 2) and 1450 cm^{-1} (peak 3) are due to C=N stretching of the imine/oxime group and C-H bending of the methyl group, respectively. Meanwhile peak at 1366 cm^{-1} (peak 4) is owing to C-N stretching from the aromatic amine compound. In addition, absorption peaks at 1218 cm^{-1} (peak 5), 1105 cm^{-1} (peak 6) and 1015 cm^{-1} (peak 7) are due to the aliphatic phosphate groups of the P=S and P=O bonds, the products of MP cleavages. Krishnaswamy [56] reported that the intense bands at 1242 cm^{-1} and 1047 cm^{-1} were from the hydrolytic cleavage

of MP and the presence of a band at 1346 cm^{-1} shows the occurrence of an aromatic NO_2 group. Similar observations were made by Yekta and Sadeghi [57] when they reacted MP with $\text{NaY}/\text{Mn}_0.5\text{Zn}_0.5\text{Fe}_2\text{O}_4$ nanocomposite, i.e, peaks at 1216 cm^{-1} and 930 cm^{-1} , are due to the presence of $\text{P}=\text{S}$ and $\text{P}=\text{O}$ bonds, and peaks at 1524 cm^{-1} and 1373 cm^{-1} indicate the presence of to the NO_2 group.

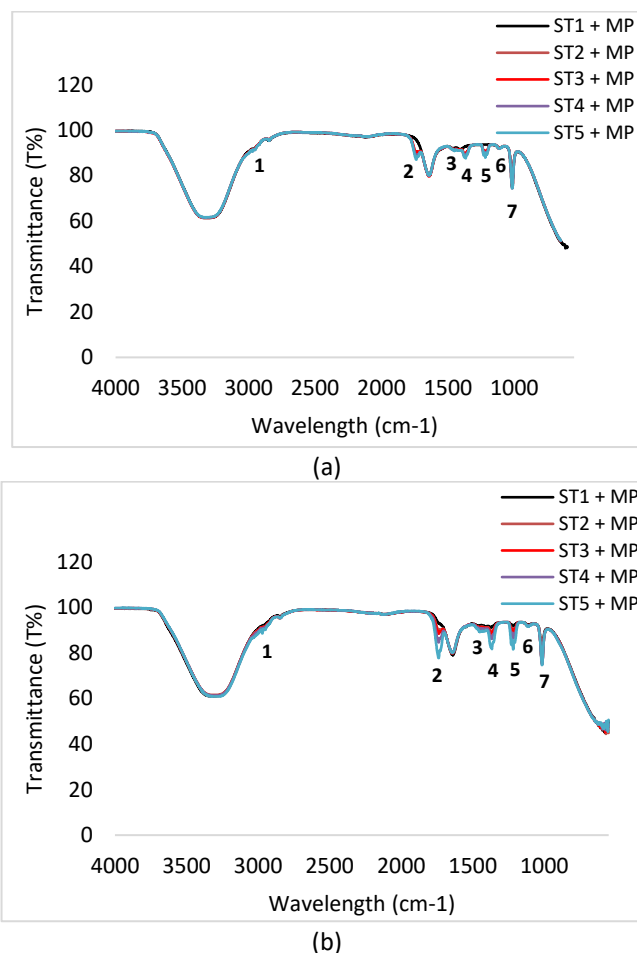


Fig. 5. ATR-FTIR spectra of liquid soaps (a) with and without oxime, and MP after 24 hours, (b) with and without 2-PAM, and MP solutions after 7 days

3.4 Organophosphate Degradation Efficacy using UV-Vis Spectrophotometry Analysis

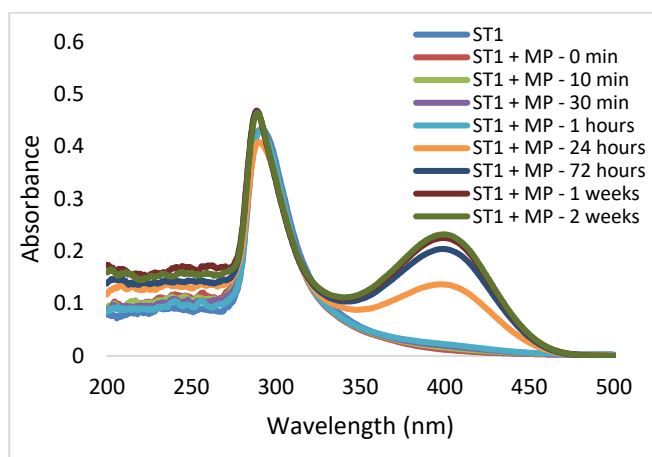
The degradation of MP and the formation of intermediate by-products was also monitored by UV-Vis spectroscopy. This technique was used by Peng *et al.*, [58] to observe the interaction of pralidoxime (PAM) and OPs.

Figure 6(a) shows the UV-Vis spectra of the solutions of the soap without oxime and MP at various mixing periods. A small shift of the absorbance the soap peak at wavelength 291.48 nm to 290.46 nm , of about 1 nm , upon addition of MP could be due to the interaction the soap and MP. The spectra of the solution at 0, 10, 30 and 60 mins of mixing period are almost identical suggesting the concentration of product from MP and soap reaction is too small to be detected by the procedure. However, at 24 hours of the mixing period, a new peak appeared at 400 nm indicating the occurrence of *p*-nitrophenol (*p*-NP) and the height of this *p*-NP peak increased as the period was increased indicating the *p*-NP production reaction period dependent under these conditions [59]. These

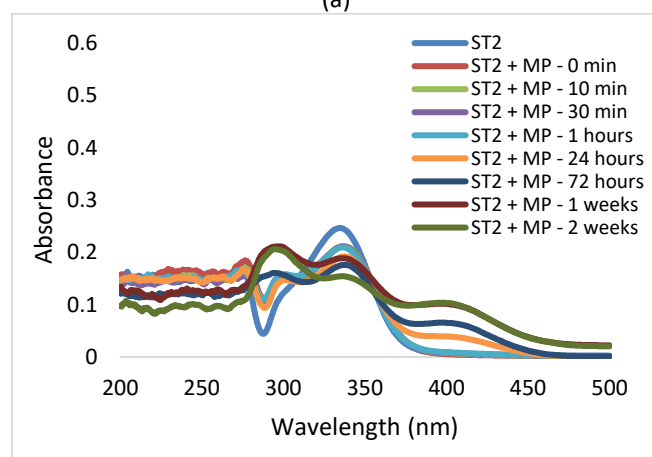
findings suggest that MP degrades in the soap solutions at a very slow rate, therefore, it requires long period to safely decontaminate the chemical.

Figure 6(b) and Figure 6(c), show UV-Vis spectra of ST2 and ST3 solutions with and without MP. UV-Vis spectra show three prominent absorption peaks that were shifted at 277 nm, 300 nm, and 337 nm, which are attributed to the formation of 2-PAM/MP complexes which are immediately formed after the addition of the MP. After 24 hours of the mixing, the absorbance of 2-PAM/MP complexes at wavelength 337 nm were decreased indicating the 2-PAM/MP complexes is consumed. Simultaneously, a new peak at 400 nm appears corresponding to the formation MP by-product, p-NP, thus supporting the degradation pathway which is by the attack of 2-PAM nucleophilic at the phosphorus atom of MP [60,61]. Noticeably, after 72 hours, a new peak was exhibits at 290 nm which substantially attributed to dimethylthiophosphate (DMPT) [13].

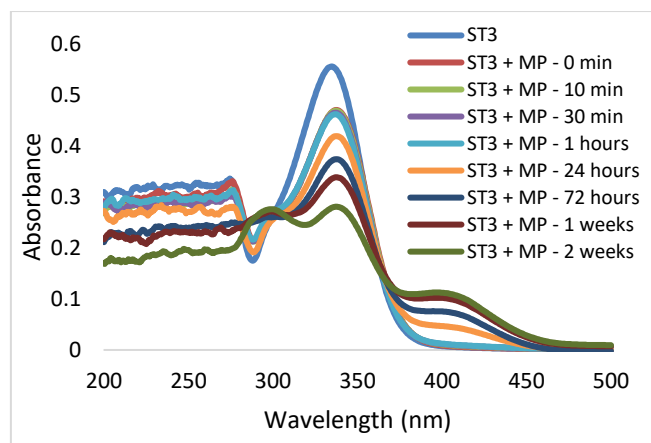
Meanwhile, Figure 6(d) and Figure 6(e) shows only one peak appeared approximately at 330 nm for the soap and oxime interaction (ST4 and ST5). The degradation of 2-PAM/MP complexes is evidenced by the reduction of absorbance over time shown at peaks of 334 nm and 337 nm, respectively. However, unexpectedly after 24 hours, there is no variation at absorbance 400 nm was observed in the spectra, which indicates there was no formation of p-NP and thus, the attack at the phosphorus atom can be ruled out for ST4 and ST5. Silva *et al.*, [13] stated that the by-product was formation of diester DMPT attributes to the degradation of MP.



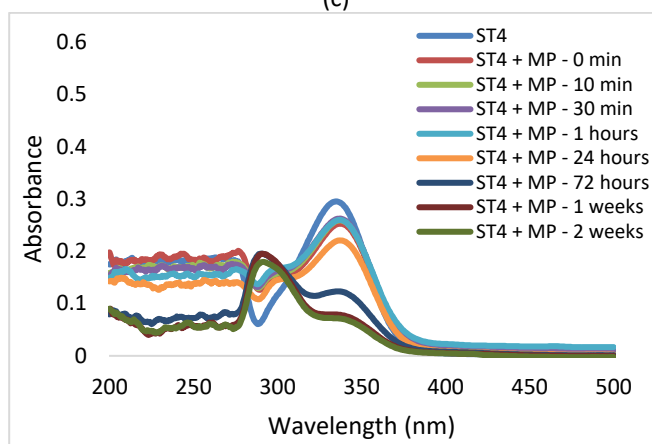
(a)



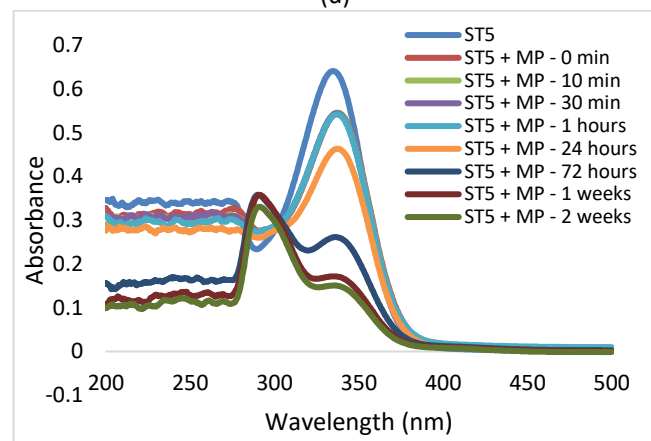
(b)



(c)



(d)



(e)

Fig. 6. UV-Vis Spectra of MP Degradation using (a) ST1,0% 2-PAM, (b) ST2,0.05% 2-PAM, (c) ST3,0.1% 2-PAM, (d) ST4,0.5% 2-PAM, (e) ST5,1.0% 2-PAM

4. Conclusions

The oxime incorporated palm oil liquid soaps with the physicochemical characteristics that are suitable to be used for MP decontaminations have been successfully synthesized. The soaps are stable at 20 °C with pH's that are just slightly higher than 11, the typical pH of the soaps that are normally used for decontamination purposes. Upon mixing the soap solutions with methyl parathion (MP), the MP degrades slowly, with the formation of p-nitrophenol (p-NP) only after 24 h. However,

in the presence of 2-pyridine aldoxime methiodide (2-PAM) with a concentration of 0.05% to 0.1%, a significant 2-PAM/MP interaction is observed, in addition to the formation of p-NP after 24h. Furthermore, at a concentration of 2-PAM of 0.5% to 1.0%, the degradation does not produce p-NP but dimethylthiophosphate (DMPT), suggesting that the oxime content in the soap is sufficient to neutralize the MP. Based on the above findings, it can be concluded that the addition of 2-PAM at the right concentration to the soaps significantly enhances their ability to efficiently decontaminate MP.

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