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Free fatty acid-rich oils as potential benign organic solvent for dyes removal in solvent extraction system

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ABSTRACT

The extensive use of water in the textile industry results in the production of significant volumes of effluent-containing dyes, posing both economic and environmental concerns due to their harmful impact. Hence, the removal of dye from wastewater is very important for environmental protection and other aspects of well-being. Solvent extraction emerges as one of the promising methods used for dye removal. Nevertheless, the conventional organic phase formulation comprises an extractant, diluent, and modifier sourced from petroleum-based compounds, leading to environmental degradation. Thus, in this study, free fatty acid (FFA)-rich oils, i.e., Palm Kernel Fatty Acid Distillate (PKFAD) and Jatropha Oil (JO), were proposed as the green and benign organic solvent for the extraction of Crystal Violet-(CV) and Methylene Blue-(MB) from an aqueous solution. These FFA-rich oils act as reactive diluents due to the presence of FFA, which acts as an acidic extractant. Therefore, a new formulation of green sole-organic solvent without the addition of extractant and modifier was applied in this system. This study aimed to determine the best *pH* equilibrium for extracting CV and MB from different FFA-rich oils, i.e., PKFAD and JO. The results indicated the optimum extraction of CV is 95% at an equilibrium *pH* of 2.7 and 6.3 for PKFAD and JO, respectively. In comparison, the extraction of MB achieved 88% (*pH* 5.5) and 86% (*pH* 8.5) for PKFAD and JO, respectively. The stripping obtained a high removal percentage for both CV and MB, with 93% and 99%, respectively.

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1. INTRODUCTION

Rapid industrialization and vast technological advancement lead to a rise in economic growth but, unfortunately, also pose significant threats to the environment and human health. Environmental contamination by wastewater from industrial effluents, particularly those containing dyes as the primary source of pollution, has emerged as a major concern in recent times. The primary sources of dyes are the industries of paint, paper, plastic, leather tanning, and textile industries [1]. Dyes are harmful materials that are also carcinogenic to aquatic organisms and humans. It is estimated that 10,000 different types of dyes are manufactured annually, and the textile industries worldwide consume approximately 7105 tonnes of synthetic dyes [2]. Even low concentrations of dyes discharged into water bodies lead to a diverse impact on aquatic life, hindering light diffusion, and slowing photosynthesis. Moreover, dyes can also irritate the respiratory tract, skin, and eyes, causing sore throats, chest pain, and severe coughs [3]. Reactive dye is the most commonly used dye in the textile industry because of its advantageous characteristics of simple application procedures, vibrant colours, and low energy usage [2]. This type of dye has a wide variety of chemical structures, primarily based on substituted aromatic and heterocyclic groups [3]. They are normally not easily destroyed; therefore, their colour persists in the effluent. Reactive dyes such as crystal violet (CV) and methylene blue (MB) have broad applications as colouring agents in textiles, plastic, cosmetics, papers, and others. Hence, the removal of CV and MB dyes is a major area of study. Numerous methods have been applied to eliminate these toxic dyes, such as coagulation/flocculation, electrocoagulation, oxidation/ozone, membrane separation, photodegradation, adsorption, and biological processes [4–7]. However, none of these methods are sufficient to achieve a simple and effective removal of dyes-loaded waste solution. Electrocoagulation processes deal with high electricity costs, while coagulation/flocculation processes consistently generate substantial amounts of sludge and require numerous chemicals. Meanwhile, membrane fouling and high operational costs pose challenges and problems in membrane filtration.

Established in the 1940s [8], solvent extraction has been widely used in many applications due to its high efficiency, simplicity, and low maintenance and operation costs [9]. In general, solvent extraction consists of the immiscible solvent of the organic and aqueous phases. The organic phase formulation comprises a diluent, extractant, and modifier. The extractant acts as the active compound to transfer the solute (dye) from the aqueous to the organic phase, and the diluent usually helps to reduce the viscosity of the extractant while the modifier improves the phase disengagement [10]. The removal of dyes in solvent extraction systems has been reported by many researchers, and the results are promising [2], [11-12]. However, the major issue in solvent extraction is the high consumption of hazardous organic solvent, i.e., toluene [11], which causes an unfavourable impact on safety and environmental issues. Meanwhile, a greener approach using fresh palm oil for dye extraction has been reported by Rahman et al. [2]. Nevertheless, this fresh palm oil only acts as a non-reactive diluent due to the lack of an extractant (active component), i.e., hydroxyl group present in the solutions. Hence, a petroleum-based extractant was added to the formulation of the organic phase, rendering the system not totally green.

A potential oil containing high free fatty acid (FFA) was explored as the benign organic solvent. FFA consists of a long hydrocarbon bond with a hydroxyl group attached at the end of the moiety, which would potentially act as the natural extractant for dye extraction. Hence, a potential benign organic solvent, namely FFA-rich oil, was proposed as a new formulation for dye removal in a solvent extraction system. Moreover, FFA-rich oils are considered non–toxic, biodegradable, and renewable, which promotes green technology in solvent extraction systems. Previously, our research team [13–16] had explored the application of FFA-rich oil, i.e., Jatropha oil (JO), Palm kernel fatty acid distillate (PKFAD), and Palm kernel fatty acid (PFAD) as the benign organic solvent for Cu(II) extraction from aqueous solutions and the results were promising. However, the utilization of this FFA-rich oil in dye extraction has not yet been explored. To the best of our knowledge, no investigation has been reported yet concerning the removal of CV and MB from waste

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solution using PKFAD and JO in the solvent extraction system. Hence, in this research, FFA-rich oil, i.e. JO (FFA=17%) [16] and PKFAD (FFA=85%), were formulated as a sole-benign organic solvent to extract CV and MB from an aqueous solution without the addition of other chemicals, i.e., modifier, diluent and extractant which are commonly used in the formulation of the organic phase in conventional solvent extraction systems.

2. METHODOLOGY

2.1 Materials and equipment

FFA-rich oils were supplied by local and foreign vendors, i.e., PKFAD by Sime Darby Sdn. Bhd. Malaysia and JO by RV Essential India were all directly used without further purification. Crystal Violet (Bendosen, ≥ 93% purity), Methylene Blue (Merck Sdn. Bhd., ≥ 75% purity), hydrochloric acid (HCl) (Fisher Scientific, ≥ 37% purity), and sodium hydroxide (NaOH) (QRëC ≥ 99% purity) were used as received.

An orbital shaker (Lab Companion, SK-300) was used to mix the aqueous and organic phases, and a *pH* meter (Hanna Instruments, HI11310) was used to measure the *pH* of the aqueous phase before and after extraction. The concentration of dyes in the aqueous phase was determined by the Ultraviolet-visible spectrophotometer (UV-Vis) (PerkinElmer, LAMBDA 25) at the maximum wavelength (λ_{max}) of 557 nm and 665 nm for CV and MB, respectively.

2.2 Solvent extraction process

The CV and MB extraction using FFA-rich oils were performed using the shake-out test [13]. In a glass-stoppered conical flask, a volume of 15 mL of the FFA-rich oils (PKFAD or JO) was added with 50 mg/L CV and MB-containing aqueous solution at a specific organic to aqueous volume ratio (O:A) of 1:1. The conical flask then was shaken for 8 minutes in an incubator shaker at 150 rpm and a constant temperature of 27 °C (room temperature). The mixture was then allowed to settle for 5 minutes to separate the organic-aqueous *ph*ase. The *pH* of the aqueous solution was adjusted using 1.0 M HCl or 1.0 M NaOH, and the *pH* of the aqueous solution was measured using the *pH* meter. If the desired *pH* was not achieved, the solution was returned to the flask, and the step was repeated until the desired *pH* was achieved. The solution was then transferred to the separating funnel for the separation of the aqueous and organic phases (settling phase). Finally, about 10 ml of the aqueous solution was taken out, and the analysis was conducted using UV-VIS to quantitatively determine CV and MB concentration. The percentage extraction (%E) of CV and MB removal was calculated using the Eq. (1):

$$\%E = \frac{DYE_{i,ext} - DYE_{f,ext}}{DYE_{i,ext}} \times 100\% \tag{1}$$

where the $DYE_{i,ext}$ and $DYE_{f,ext}$ are the initial and final concentrations of the dye respectively, in the aqueous extraction phase. All the extraction experiments will be carried out in duplicate at 27 °C, and the relative standard deviation between replicate samples should be within an experimental range of less than 4%. Fig. 1 illustrates the solvent extraction and settling process of dye from aqueous solutions.

The stripping process or back extraction was run using HCl as the stripping agent. The stripping experiments were conducted using the same procedures as the extraction experiments, except the *pH* adjustment was skipped. An organic-to-aqueous volume ratio of 1:1 and a temperature of 27 °C were applied throughout all the stripping experiments, and the molarity of the HCl used was 1.0 M. The percentage of stripping (%S) of the dyes is in Eq. (2) as follows:

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$$\%S = \frac{DYE_{f,strip}}{DYE_{i,ext} - DYE_{f,ext}} \times 100\% \tag{2}$$

where the $DYE_{f,strip}$ is the final concentration of dye in the aqueous stripping phase. All the stripping experiments will be carried out in duplicate or triplicate with the relative standard deviation between the replicate samples within the experiment range of less than 4%.

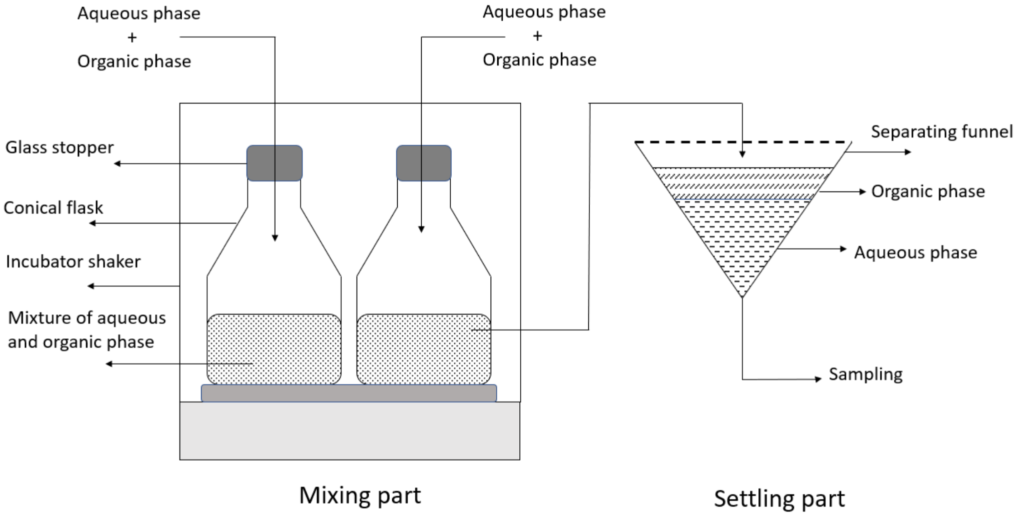

Fig. 1. Solvent extraction and settling process of CV and MB from aqueous solution

3. RESULTS AND DISCUSSION

3.1 Effect of equilibrium *pH* on dye extraction

An equilibrium *pH* (pH_{eq}) extraction is the most significant parameter to evaluate the behaviour of solute transfer from an aqueous to an organic phase in a solvent extraction system. Fig. 2 shows the effect of pH_{eq} (2.0-9.0) on the extraction of CV (Fig. 2 (a)) and MB (Fig. 2 (b)) from aqueous solution in both the PKFAD and JO systems. The %E of CV with PKFAD was found to increase from 88% to 95% at pH_{eq} of 2 to 2.7 and then slightly decrease to 93% and 84% at pH_{eq} of 3.7 and 4.6, respectively, before dropping to 32% at *pH* of 5.7. Meanwhile, the %E of CV with JO increased from 66% to 94% at *pH* of 2.3 and 4.7 and then reached optimum (95%) at *pH* 6.3 before declining afterwards with the rise of pH_{eq}. Meanwhile, the %E of MB with PKFAD was drastically increased at *pH* of 2.2 (71%) to 5.5 (88%) and declined afterwards with the increment of pH_{eq}, while similar trends were observed for the MB-JO system where the optimum pH_{eq} reach at 8.5 with the removal of 86%.

In general, the results show a high pH_{eq} dependency of PKFAD and JO on both CV and MB extraction. This could be explained by the high FFA content in PKFAD (FFA=85%) [16] and (JO) (FFA=17%) [16], which act as the active component for the extraction process [12]. Both CV and MB are cationic dyes, which are positively charged compounds, as shown in Fig. 3 below.

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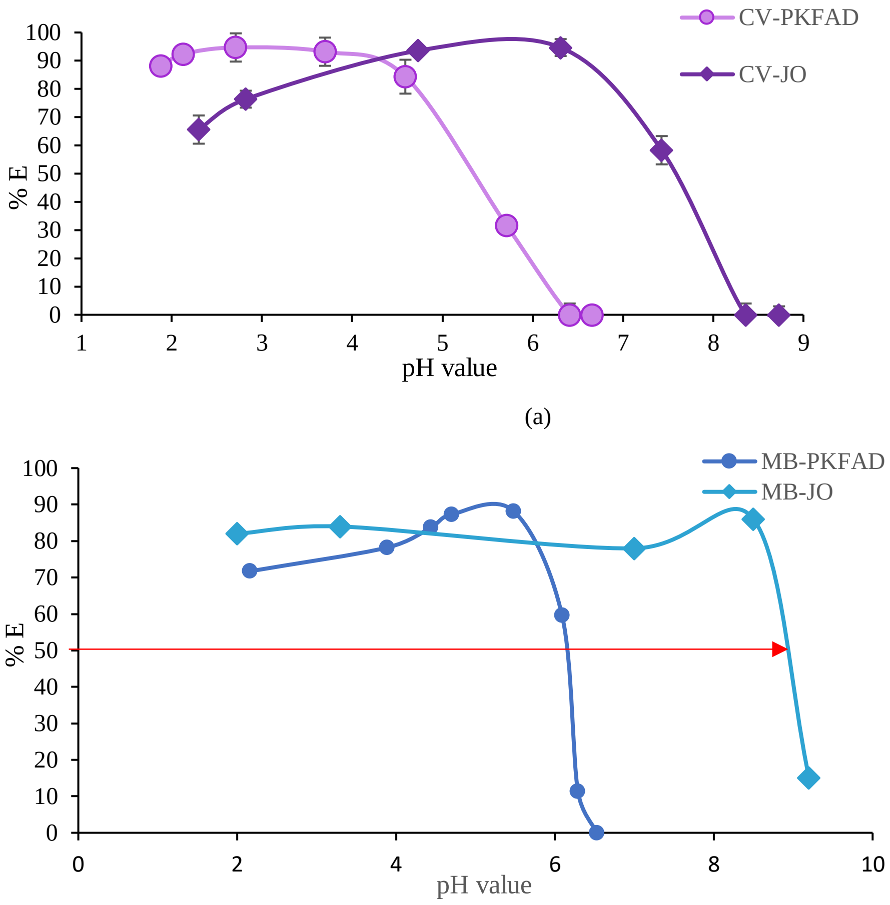
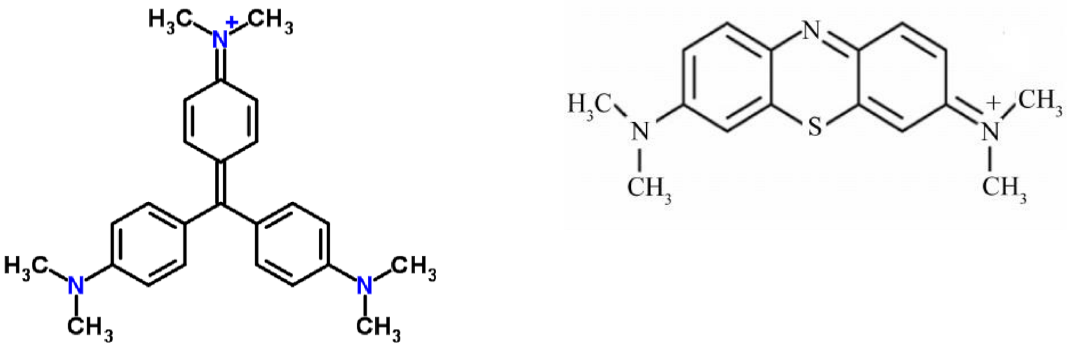


(a)

(b)

Fig. 2. Effect of equilibrium *pH* on (a) CV and (b) MB extraction in both PKFAD and JO system



(a)

(b)

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Fig.3. Chemical structure of (a) CV and (b) MB

The free OH group from the FFA is protonated, with the H^+ leaving the organic phase and the negative charge of O^- attracting the positively charged cationic dye (N^+) via cation exchange to form dye–FFA complexes [12]. As the extraction proceeded, more extractant species were formed while the H^+ were released to the aqueous phase, as shown in the Eq. (3) below:

$$Dye + FFA \leftrightarrow Dye - FFA + H^+ \tag{3}$$

This may explain the increment trend of %E for CV and MB in both systems at lower *pH*, where the extraction equilibrium proceeds to the right side with the reduction of H^+ (increasing *pH*) [16]. However, a further rise in the *pH* led to the reduction of %E of CV and MB for both PKFAD and JO systems. This could be deduced from soap formation due to the addition of NaOH during the *pH* adjustment at higher *pH* values. The presence of this soap acts as a surfactant to stabilize the emulsion layers by reducing the liquid – liquid interfacial and prolonging the emulsion breaking time, thus deducing the mass transfer of dyes from the aqueous to organic phase [16]. On the other hand, the equilibrium *pH* isotherm for both the CV- and MB-PKFAD systems was observed to shift more to the left side compared to the CV- and MB-JO systems. This implies that PKFAD is a stronger acidic extractant compared to the JO, with the former performing better at acidic conditions with a pH_{50} (50% of solute was extracted) of 5.3 (CV) and 6.3 (MB). The latter exhibited well at slightly alkaline conditions with a pH_{50} of 7.6 (CV) and 9.0 (MB) [17].

3.2 Stripping process from dyes-loaded PKFAD

Recovery of CV and MB from binary dyes loaded PKFAD were run at a 1:1 volume ratio of organic to aqueous *ph*ase. Fig. 4 depicts the results for the %S of CV and MB using 1.0 M HC1. The results reveal the high %S was achieved at 93% and 99%. According to Eq. (3) (Section 3.1), the increment of the proton, H^+, released by the stripping agent HCl, shifted the equilibrium to the left side. The dye-organic complexes (dye-FFA) react with H^+, releasing 1 mol of dye while generating FFA back into the solution. The stripping process enables the organic solvent PKFAD to be reused, minimising operating costs and promoting sustainability in the dye's recovery process.

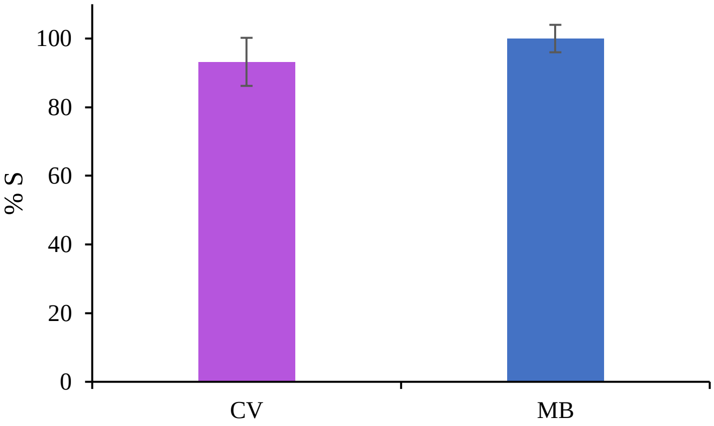

Fig. 4. %S of CV and MB using 1.0 M HCl as stripping agent

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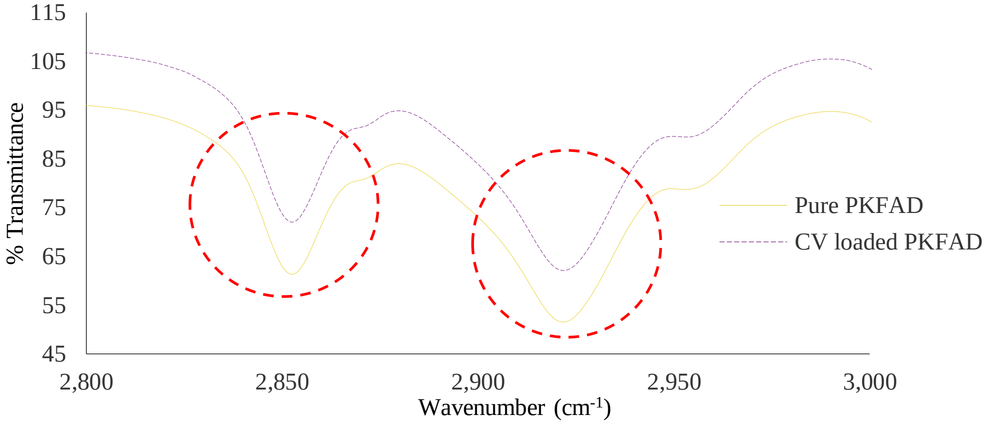
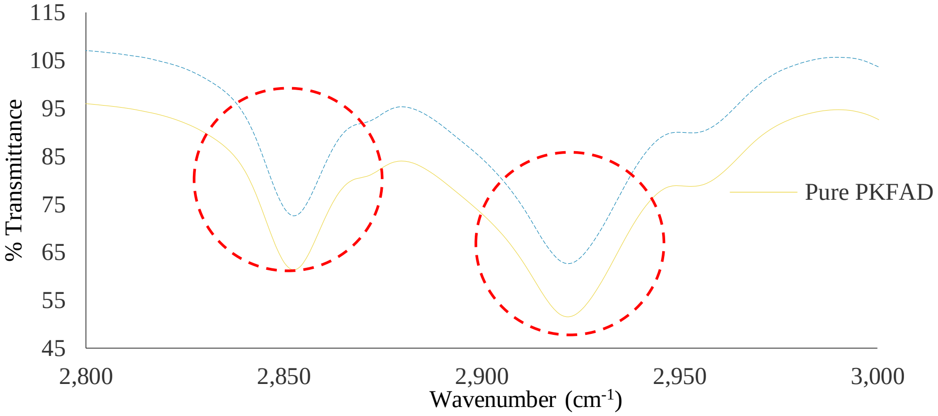
3.3 FTIR analysis

The presence of CV- and MB-FFA complexes (extracted species) in PKFAD was confirmed using the FTIR analysis. Two samples, PKFAD before and after dye extraction, were taken for the analysis. The sample before extraction contained pure PKFAD, while the sample after extraction contained CV and MB-loaded PKFAD. The FTIR spectra obtained are presented in Fig. 5 for (a) CV-PKFAD and (b) MB-PKFAD system. Both Fig.5(a) and Fig. 5(b) revealed the spectra intensity of a strong absorption peak at a wavelength of 2800-3000 cm^{-1}, which is assigned to the hydroxyl (OH$^-$) stretch of a carboxylic acid [18] is higher for the PKFAD sample before dye extraction compared to PKFAD sample after dye extraction. The former could be explained by the presence of more carboxylic components due to the absence of a dye extraction process [19]. However, the latter has fewer carboxylic components due to the cleavage of the hydroxyl group (OH$^-$) to react with the dyes through the cation exchange process, reducing the intensity of the hydroxyl (OH) stretch of the carboxylic [16].



(a)



(b)

Fig. 5. FTIR spectra of PKFAD before and after (a) CV and (b) MB extraction

4. CONCLUSION

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The green organic solvents of PKFAD and JO were successfully formulated as a sole-organic solvent for the removal of CV and MB. PKFAD extracted 95% and 88% of CV and MB at optimal *pH* equilibriums of 2.7 and 5.5, respectively. Meanwhile, JO was able to extract 95% and 86% of CV and MB at optimal *pH* equilibriums of 6.3 and 8.5, respectively. The back extraction from the dye-loaded PKFAD of 93% and 99% were achieved for CV and MB, respectively. The presence of the extracted species, i.e., CV-FFA complexes and MB-FFA complexes, was verified using the FTIR analysis. Hence, this sole-organic system would minimize the utilization of petroleum-based organic solvents commonly used in conventional solvent extraction. Moreover, this approach could benefit the environment and would promote sustainability in solvent extraction systems.

5. ACKNOWLEDGEMENT

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6. CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare the absence of conflicting interests with the funders.

7. AUTHORS’ CONTRIBUTIONS

Siti Fatimah Abdul Halim: Conceptualization, investigation, methodology, data collection, data analysis, writing- original draft preparation, editing, and supervision**; Siti Aishah Yusuf**: laboratory work and data collection; **Siu Hua Chang**: Writing- original draft preparation and supervision, **Nurulhuda Amri**: Reviewing and editing.

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