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Short communication

Recovery of oil and carotenes from palm oil mill effluent (POME)

A.L. Ahmad*, C.Y. Chan, S.R. Abd Shukor, M.D. Mashitah

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Prai Selatan, Pulau Pinang, Malaysia

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ABSTRACT

Recovery of oil and carotenes from palm oil mill effluent (POME) was investigated in this paper. Solvent extraction was used to recover the residual oil from POME on a batch basis and silica-based resin was used in the column chromatography to separate the carotenes from the recovered oil. Residual oil extracted from POME in this study was 1710 mg/L by using petroleum ether and 3280 mg/L by using *n*-hexane in a single stage of solvent extraction. The carotene content in it was about 400 ppm. Carotenes from the recovered oil was then separated to α-carotene and β-carotene at a concentration of about 1450 ppm by column chromatography. The major components of recovered oil from POME were similar to the crude palm oil, which contained mainly α-carotene and β-carotene.

1. Introduction

Crude palm oil (CPO) is the world's richest natural plant source of carotenes in terms of retinol. CPO possesses 1% minor components which amongst them are the carotenoids, vitamin E (tocopherols and tocotrienols) and sterols. The orange colour of palm oil is due to the presence of these carotenes. Its concentration normally ranges between 400 and 3500 ppm and it contains about 15 times more retinol equivalents (vitamin A) than carrots and 300 times more than tomatoes [1]. The major carotenes in palm oil are α- and β-carotene, which account for 90% of the total carotenes [2]. Carotenes, in particular β-carotene is the most important vitamin A precursor in human nutrition as they can be transformed into vitamin A *in vivo* [3] and provides the major source of vitamin A for third world populations, particularly in Asia and Africa [1,2]. β-Carotene also helps to prevent night blindness, eye problems and skin disorders, it also could enhance immunity and protects against toxins, colds, flu and infections. The importance of carotenoids has also increased due to the more extensive use of natural compounds in the food, cosmetic and pharmaceutical industries. Since carotenoids are expected to grow in importance and value, their recovery from palm oil and its by-products is important.

About 50% of water used in the palm oil extraction process will result in palm oil mill effluent (POME) while the other 50% will be lost as steam. POME is a high volume liquid wastes which are non-toxic, organic in nature but have an unpleasant odour and are highly polluting. It is originated from the mixture of a sterilizer condensate, separator sludge and hydrocyclone wastewater [4]. About 2.5 tonnes of this waste was produced for every tonne of oil extracted in an oil mill [5]. The standard discharge limit for oil and grease according to Environmental Quality (prescribed premises) (crude palm oil) Regulations 1977 is 50 mg/L while the concentration of oil and grease in POME is about 6000 mg/L. The oil droplets of POME can be found in two phases, being either suspended in the solids or floating in the supernatant. These residue oil droplets are solvent extractable [6]. Due to the readily available source of POME and growing value of carotenes, the objective of this study was to extract the oil from POME using solvent extraction on a batch basis and separation of the carotenes from the recovered oil through a single-stage chromatographic process. Silica-based resin was used in the adsorption chromatography. Although some studies have been done on oil extraction from POME, but extracting carotene from POME and separation of carotenes from the recovered oil through adsorption chromatography have never been done.

2. Materials and methods

2.1. Materials

POME samples were collected from United Palm Oil Mill, Nibong Tebal at temperature of 80 °C. All solvents and chemicals used were of analytical grade. Silica gel was obtained from Sigma–Aldrich (M) Sdn Bhd, Malaysia. This silica gel has a particle size of 63–200 μm.

2.2. Solvent extraction

Extraction of oil with different ratio of solvent-POME was done at room temperature, 28 °C. 200 mL sample of POME was mixed

* Corresponding author. Tel.: +60 4 5941012; fax: +60 4 5941013.
E-mail address: chlatif@eng.usm.my (A.L. Ahmad).

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with the volume of solvent increased by 40 mL for every experiment until the ratio of solvent to POME reached 1:1. The solvent and POME were mixed in a flocculator for 10 min at 150 rpm. The contents were then transferred to the separating funnels and left to separate into two layers. The extract was filled into a conical flask and solvent was distilled off using rotary evaporator. The drying process was conducted in an oven at ∼102 °C for 15 min. The flask was cooled in desiccator for 30 min and then weighed using a four digits electronic balance. The measured weight was taken as oil and grease content value.

2.3. Adsorption column chromatography

The chromatography column used was 200 mm in length with 20-mm internal diameter. Adsorbent was packed in the column and the study was done at room temperature. 10 g of extracted oil was dissolved with 30 mL *n*-hexane and then loaded onto the column chromatography to contact with adsorbent. A non-polar solvent, 170 mL *n*-hexane was then brought into the column. A mixture of solvents, 100 mL of ethanol/*n*-hexane (50:50, vol/vol) was later added to the column chromatography. Fractions of 12 mL eluent were collected regularly in receiving flask. The oil content of each fraction was then determined gravimetrically after removal of the solvent by a rotary evaporator. The carotenes content was determined by using spectrophotometer Genesys 20 at 445 nm. 0.1 g of the sample was dissolved in 25 mL *n*-hexane according to PORIM test method [7].

2.4. Carotenes analyses

Carotenes in oil samples were determined by using high performance liquid chromatography (HPLC). The HPLC system used was equipped with SPD-10A UV–vis detector from Shidmadzu, Japan with a 150 mm × 4.6 mm Inertsil 5 μm ODS-3 column. The measurements conditions are at absorbance of 450 nm and at column temperature of 40 °C. The mobile phase used was acetonitrile/ethanol (7:3, vol/vol) at a flow rate of 1 mL/min and analysis time of 25 min.

3. Results and discussion

3.1. Solvent extraction

Fig. 1 shows the effect of solvent ratio to POME on the extraction of oil from POME. A trend was observed where the oil concentration increased as the amount of solvent increased. However, after a certain amount of solvent, the increase in concentration of recovered oil was relatively small and became constant. This phenomenon indicated that at ratio of 0.6, the extraction process had almost reached the saturation value. The result obtained was comparable with the previous work [8], where the ratio also became constant at 0.6 as the stability of the emulsion formed decreased the ability of solvent to extract the oil [9]. Hence, the solvent to POME ratio at 0.6 was the optimum solvent ratio value for the current extraction process.

The highest oil and grease content that could be recovered from POME was about 3280 mg/L for a single batch extraction using *n*-hexane and 1710 mg/L by using petroleum ether. The initial concentration of oil and grease in POME was 4610 mg/L which means that 71.1% and 37.1% of the oil and grease could be recovered from POME by using *n*-hexane and petroleum ether, respectively. According to Fig. 1, oil concentration extracted using petroleum ether was always less than the oil concentration extracted using *n*-hexane. Therefore, the result also indicated that *n*-hexane was a better organic solvent to extract the oil and grease content from POME compared to petroleum ether.

Fig. 2 demonstrates the effect of solvent to POME ratio on carotene concentration of the extracted oil from POME. The carotene concentration in the recovered oil distributed evenly although the solvent ratio was varied. This revealed that the ratio of solvent did not influence much on the carotene concentration in the recovered oil. The mean concentration of carotene in oil extracted by petroleum ether was 417.9 ppm, whereas the mean concentration of carotene in oil extracted by *n*-hexane was 394.8 ppm. The petroleum ether used in this study had boiling point of 40–60 °C whereas the boiling point for *n*-hexane was 69 °C. Therefore, higher temperature was needed to evaporate the *n*-hexane from the recovered oil and this might cause thermal decomposition of carotenes in it and resulted in lower carotene concentration value for *n*-hexane.

Non-polar solvents were used in this study to extract the carotenes from POME because polar solvents such as acetone, methanol and ethanol are good for extraction of xanthophylls but not for carotenes [10]. Furthermore, the content of xanthophylls in palm oil is very low which is only 2.2% compared to 97.8% for carotenes [1]. The polar solvents are also soluble in water and this type of extraction will not show a distinctive layer between the oil phase and POME compared to the extraction by using non-polar solvents which are immiscible with the POME.

3.2. Adsorption column chromatography

Fig. 3 is the adsorption column chromatography for separation of carotenes from recovered oil of POME by using silica gel with the initial solvent of hexane and second solvent of ethanol/*n*-hexane. The amount of eluted oil for every fraction was plotted in the same figure with the diagram of carotene concentration for every fraction. From Fig. 3, it can be seen that there are two sharp peaks on the chromatogram for the amount of eluted oil and one sharp peak

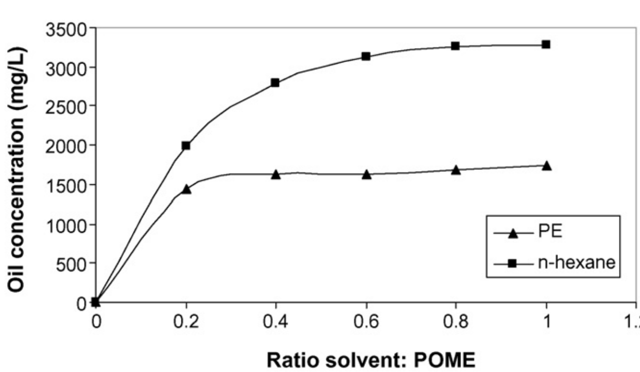

Fig. 1. Effect of solvent-POME ratio on extraction of oil.

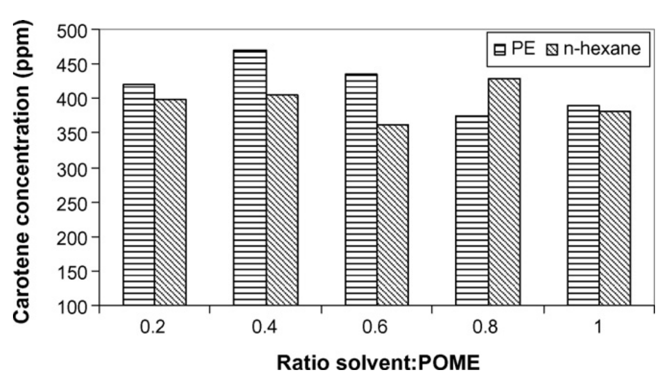

Fig. 2. Effect of solvent-POME ratio on carotene concentration (ppm) of the recovered oil.

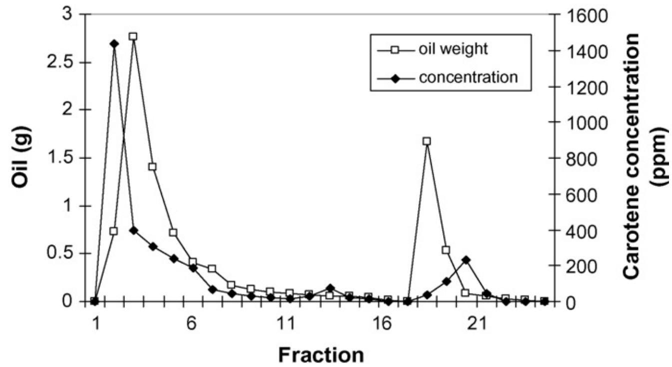

Fig. 3. Adsorption column chromatography for separation of carotenes from recovered oil of POME.

for the carotene concentration. The recovered oil was concentrated to 1450 ppm at the second fraction and decreased afterward. This was mainly because the carotene did not adsorb on the adsorbent and was eluted by hexane whereas most of the triglyceride in it was adsorbed on the adsorbent. The liquid mobile phase provided transportation to the sample as a carrier, but more importantly, it influenced the distribution coefficient through its solvent power. In addition to the relative solubilities of the solutes in the eluting solvent, it was also necessary to consider the competition between the solutes and solvent for the adsorption sites on the surface of the stationary phase [11].

From Fig. 3, the first peak for the amount of eluted oil occurred at fraction 3 and the second peak appeared at fraction 18. This phenomenon was due to the introduction of recovered oil to the column by only one loading at the beginning of the process and the oil content did not manage to strongly adsorb on the adsorbent and was carried away by the mobile phase and eluted in a high amount during fraction 3. This could also be explained by the surface activity of the adsorbent which was largely lost when it was covered by a monolayer of the adsorbed species. The second solvent was introduced just before fraction 18 and caused the occurrence of the second sharp peak. This indicated that the remaining triglyceride in the recovered oil was eluted by ethanol. Ethanol was chosen rather than methanol because of the slow elution of oil due to poor solvency in methanol [12]. Besides, Zang et al. [13] showed that the absorbance of β-carotene in hexane was larger than in methanol and β-carotene was present as monomers in hexane and crystals might likely form in methanol at higher concentrations. Therefore, most of the carotenes were eluted by *n*-hexane in fraction 2 rather than the second solvent which was a mixture of ethanol and *n*-hexane.

This column chromatography had concentrated the carotene content from about 390–1450 ppm, which was four times of the original concentration. The total amount of carotenes in fraction 2 was 1048 mg whereas fraction 3 had 1091 mg of carotenes. These had contributed to the recovery of carotenes in fractions 2 and 3 as 34.8% and 36.3%, respectively. However, the amount of solvent used to dissolve the recovered oil loading should be adjusted to achieve the peaks for both amount of eluted oil and carotene concentration at the same fraction.

According to Latip et al., the carotene was concentrated to about 25 times of the original concentration in CPO by adsorption process using synthetic adsorbents followed by solvent extraction [14]. The concentrated carotene obtained from POME is small compared to concentrated carotene obtained from CPO. This may due to different types of adsorbents, adsorbents/CPO ratios and solvents used in the process. By optimizing these parameters, higher concentrated carotene can be obtained from POME. Owing to vast amount of POME generated as waste, this waste will certainly have a significant impact on the environment if they are not dealt with appropriately. Therefore, it is viable to recover the oil and carotenes from POME.

3.3. Carotenes analyses

Fig. 4 shows that HPLC analyses of carotenes in crude palm oil was almost the same trend as in recovered oil from POME. The major components of recovered oil from POME were similar to that from crude palm oil, which contained α-carotene and β-carotene. This was mainly because the recovered oil from POME was originated from sterilizer condensate and sludge separator discharge in the palm oil mill.

Ibrahim and Kuntom reported that the range of carotene for sludge palm oil (SPO) was 7.7–678.2 ppm with a mean value of 241.4 ppm [15]. According to Fig. 2, the mean value of the carotene from POME was higher than the mean value of carotene for SPO. This might be due to spillage of CPO into sterilizer condensate or high wear and tear in the machine parts during the extraction process. Besides that, the percentage for β-carotene was much higher than α-carotene which was 65%:35% and 70%:30% in CPO and oil extracted from POME, respectively. The ratio was almost the same for the ranges in content for carotenoids in the unsaponifiable fraction from a palm oil where β-carotene:α-carotene was 54.4%:36.2% which accounted for 90% of the total carotenoids [1]. Mortensen also reported β-carotene:α-carotene was in the ratio 3:2 which constituted the major part of the carotenes [16].

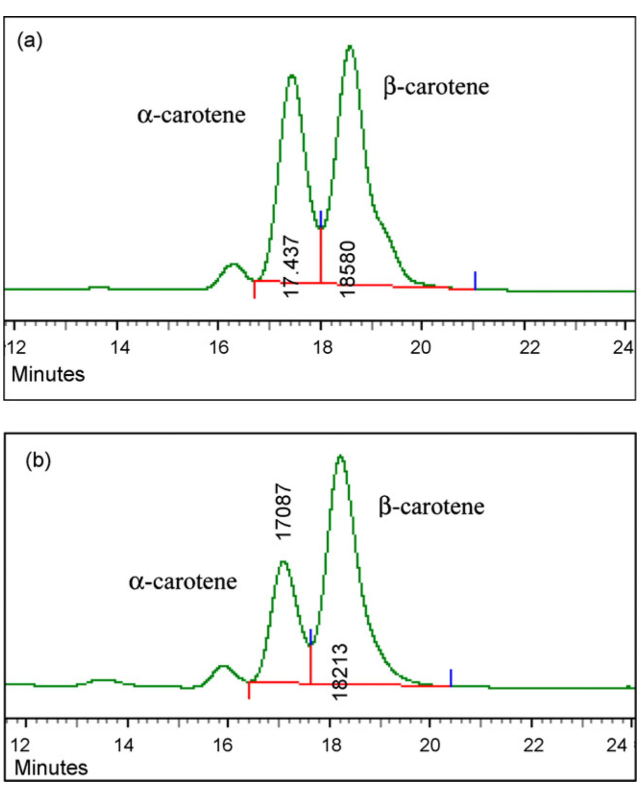

Fig. 4. High performance liquid chromatography (HPLC) chromatogram of α-carotene and β-carotene in crude palm oil (a) and recovered oil from POME (b).

4. Conclusions

The solvent to POME ratio of 0.6 was the optimum solvent ratio value for the extraction of oil from POME. The highest oil and grease content that could be recovered from POME for a single batch extraction using *n*-hexane was 3280 mg/L and 1710 mg/L by using petroleum ether. *n*-Hexane was a better organic solvent to extract the oil and grease content from POME compared to petroleum ether in this process. The adsorption chromatography had concentrated the recovered oil from 390 to 1450 ppm carotene. Besides, the major components of recovered oil from POME were similar to those of the crude palm oil, which contained α-carotene and β-carotene. The percentage for β-carotene was much higher than α-carotene which was 70%:30% in oil extracted from POME. This suggested that oil could be recovered from POME by using *n*-hexane in solvent extraction process and carotenes could be separated and concentrated by adsorption chromatography.

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