Analysis of Oil Content in Ultrafiltered Water Based on Oil Emulsion using Fourier Transform Infrared Spectroscopy (FTIR)

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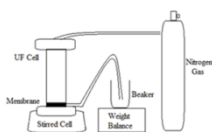
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Graphical abstract

Abstract

The quantitative analysis is a simple and fast method that has been developed to analyse the oil content in the permeate of ultrafiltration process. Measurements of concentration were done on standard palm oil solution within 0.05–7.00 wt. %, followed by verification of permeate content to validate the calibration model. The measurement was based on simple Beer's Laws method to determine the concentration of oil in the permeated water. The standard oil solution was analysed using Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) to obtain the spectrum of triglycerides group, which are the principal component that exists in fats and oils. The absorption wavelength was found to be within 1789.62 cm^{-1} and 1697.53 cm^{-1}. The selected region will be used to quantify the standard oil concentration. Regression coefficient (R^2) for the calibration model and validation was 0.99267 and 0.9913, respectively indicating excellent oil concentration determination. These results showed that all the measurements were in the range of calibration curve which shows a facile method is suitable for the oil determination in the permeate water samples. The ATR-FTIR method was compared with turbidity method, thus ATR-FTIR method was preferred and reliable to be used in determining of oil concentration.

Keywords: Oil concentration; quantitative analysis; extraction; Fourier Transform Infrared Spectroscopy; calibration curve; ultrafiltration process

■1.0 INTRODUCTION

The insoluble component of wastewater comprises various natural and petroleum organic compounds. Currently, most analytical methods in analyzing the waste water quality are rarely focused on the specific substances or compounds. As a result it becomes a regulatory issue when these substances are being discharged into the river. There are many methods that have been developed in verifying the substances existence in the effluent streams [1]. The discovery of oil and grease (O&G) clogged or detracted from the treatment plants initiated the analytical measurement of oil content. Even though, numerous biological treatments such as anaerobic digester have been done, existing occurrence of greasy scum layer that prevents gas transferring and mixing leads to total disruption of the process. Therefore, the O&G was further analysed by using common analytical techniques. Table 1 shows common analytical techniques and its improvement since 1977s.

Due to incompetency of the old methods, new methods have been developed. The methods are:

a) Alum coagulation pre-treatment followed by filtration, extraction of the filtered oils and extraction with petroleum ether for 16 hrs [3].
b) Acidification and refrigeration as pre-treatment followed by filtration, extraction of the filtered oil and drying [4].
c) Liquid-liquid extraction of an acidified sample followed by separation and drying of the extract [5].
d) Pre-treatment by lime coagulation followed by filtration, modification of filtered oil, fluffing, and extraction for four hour [6].
e) Oil extraction of sewage solids or sludge followed by extraction of the oil [7].

Table 1 The earliest analytical method [2]

Method	Process description	Disadvantage
Hazen's method	A 500 ml of oily waste water was evaporated to 50 ml, and followed by neutralization with hydrochloric acid. It's was evaporated until dry and further extracted with solvent. The solvent was then leave to evaporate. The dried weight reported as O&G.	Time consuming and often produce inconsistent results.
Knechtges	A modification from Hazen method. They used Caldwell extractor to extract the residue from evaporating sample. They also investigated the types of compounds which are present in the extract.	Time consuming and used solvent with high flammability.

These five new methods required high toxicity solvents such as petroleum ether and chloroform where the water takes longer time to evaporate. The loss of low molecular fraction of oil during evaporation process is the error found in this stage. Besides that, another common error caused by the processes is the inability to extract high percentage of the fatty acids due to the formation of insoluble precipitates in the dried residues. This especially happens at neutral pH. Conversion of the precipitates into organic acids in acidic treatment of the filtered oil is a way to overcome the errors.

Methods of analyzing oil from wastewater are keenly developing as time passed by to ensure the extraction efficiency. Therefore, Pomeroy [5] proposed an improvement of liquid-liquid extraction method. N-hexane [8] and Freon 113 (1,1,2 tri-chloro-1,2,2 trifluoroethane) has been introduced to replace chloroform and petroleum ether as a solvents [9]. Unfortunately, n-hexane is quite flammable and for this reason other non-flammable solvents were needed. Meanwhile, Freon 113 is preferred because it is not flammable and at the same time gives the same efficiency as n-hexane.

Based on previous studies, Gruenfeld [10] found that the extracted oil can be measured by infrared (IR) spectrophotometer. The use of IR radiation could overcome two important problems. First, it extends the nominal limits of detection of oil to level of 10 ml. Next, the evaporation of solvent was not required in the IR spectrophotometer technique, which could reduce the loss of low molecular weight compounds.

IR spectroscopy is not an analytical method that is commonly associated when analyzing water. It can be used for various samples which consist of many substances or compounds. Therefore, it is a powerful tool to quantify organic chemicals and identify the chemical structure of the molecules investigated [11]. The chemical bonds from specific component will vibrate once stimulated by IR radiation (Russell, 2005). It also predictably resonates at frequencies related to each bond of energy. The frequency spectra of IR radiation will exhibit absorbance at specific wavelength depending on the structure of the chemical.

So far, there is no analysis of oil content in permeated water from UF is found in recorded studies. Recently, turbidity method is often used to determine the oil concentration of the permeated water [12]. Unfortunately, this method is not effective as it could not determine a minimum value of oil concentration. This is because it only measures the existence of suspended solids in the water. Therefore, by combining these two methods (extraction and radiation), the aim is to calibrate the oil emulsion concentration and its effluents after filtration process. This

calibration model will expected could be used to determine the oil concentration of UF process for future researches. The calibration process was done by measuring the IR spectra for palm oil in order to identify any chemical nature of the sample. Solvent that is hydrophobic in nature was chosen in order to absorb all the water from the samples. This is because water strongly absorbs IR radiation and effectively masks the IR absorption bands. It also might interrupt the absorption of sample through IR spectra thus, resulting in poor performance.

In determining the concentration of the oil content in permeated water, a simple quantitative method by using Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) was practised. Beer's Law was used to analyze the oil concentration in permeated water. Toluene, one of the organic solvent, was used to extract the oil residues from the water permeated sample. After that, the sample was measured using ATR-FTIR method to determine the concentration of oil. Later on, the results obtain were compared between ATR-FTIR method and turbidity method in order to evaluate measurement of oil content.

■2.0 EXPERIMENTAL

2.1 Instrument

The instrument used to quantify the oil concentration was Thermo Scientific Nicolet iS10 FTIR spectrometer with IR range within 4000 to 400 cm^{-1}. The spectra will be quantified and collected using Attenuated Total Reflection (ATR) accessory having zinc-selenium (ZnSe) with crystals at an angle of 45°. All spectra were collected at 4 cm^{-1} resolution using DTGS KBr detector. Then sample was scanned for 32 times and IR spectrum was interpreted by using TQ Analyst software. Root mean standard error of prediction (RMSEP) was calculated during calibration in order to identify the ability of the method in predicting the concentrations of each components in the validation standard.

2.2 Quantitative Analysis

All standards were prepared from oil palm cooking oil. Eight oil standard solutions were prepared to develop the calibration curve of ATR-FTIR. The standard oil samples were first scanned to determine the significant functional group. The solutions were prepared by weighing an appropriate amount of oil and toluene. The concentrations of the standard oil solutions were listed in Table 2. Both of them were mixed together in a beaker and continuously stirred at a speed of 150 rpm for 25 minutes. This is continued until the toluene completely extracts the oil residue. These standard solutions were then analyzed using ATR-FTIR.

Table 2 The concentration of standard oil solutions for calibration model

Oil (g)	Toluene (g)	Oil concentration (wt%)
0.05	9.95	0.5
0.10	9.90	1.0
0.20	9.50	2.0
0.30	9.00	3.0
0.40	8.50	4.0
0.50	8.00	5.0
0.60	7.50	6.0

2.3 Oil Emulsion Filtration Process

A dead end stirred cell filtration system (STERLITECH High Pressure Stirred Cell) connected with a nitrogen gas line and solution reservoir was designed for the synthetic oil emulsion filtration process. An optimized membrane with compositions of 15 wt. % of PSf, 2 wt. % of SiO2 and 1 wt. % of PVP was used to filter the oil emulsion. The system consists of filtration cell with a volume capacity of 200 mL and inner diameter of 62 mm. The effective area of the membrane was 13.86 cm^2. Nitrogen gas was used as driving force of the feed system. Figure 1 show apparatus setup for UF process. Experiments were carried out at different concentration of oil ranging from 0.5 wt. % to 7 wt. %. The permeated water flux at different concentration of feed stream was collected during UF process in order to identify the final oil content. These samples would later on used as the standard in verification of calibration curve.
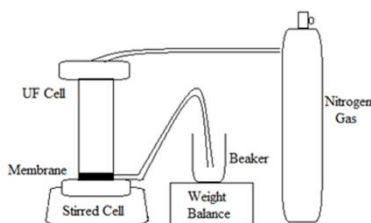

Figure 1 Apparatus set-up

2.4 Permeate Water Sample Preparation

For validation set, 5 g of permeated water samples were measured and dried in the drying chamber at 90ºC for 2 h. The particular temperature was used to avoid the loss of any low molecular weight fraction of the oil during evaporation process. Therefore, slow heating was preferred in removing the water. After that, the dried oil from sample solution was left to cool down to reach room temperature. Then, the toluene was added to extract dry oil residues until the total weight of 10.

For turbidity method, both oil emulsion and permeated water flux were determined by using Lovibond Portable Turbidity Meter. 15 mL of samples was poured into vial and left in the turbidity checker for 5 minutes. The process was repeated three times for each sample. The average of turbidity was then calculated.

■3.0 RESULTS AND DISCUSSION

3.1 Qualitative Analysis

FTIR was used to identified any components exist in the samples. Palm oil basically contains a lot of fats and oil [13]. Most of the peaks and spectrum of fats and oils corresponds to the specific functional groups. Normally, triglycerides are principal components that exist in fats and oils [14]. Figure 2 shows the IR spectroscopy for palm oil cooking oil ranging from 4000 cm^{-1} to 400 cm^{-1}. Table 3 contains peaks and its related functional groups in the palm oil especially, at wavelength of 1743 cm^{-1} which represents triglycerides group in palm oil [15]. The study was focused on the triglycerides group due to its domination.
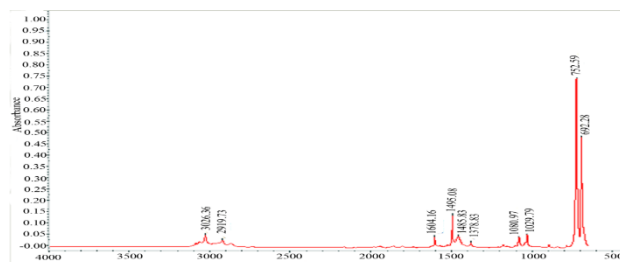

Figure 2 FTIR spectrum of palm oil

In the phloem, sieve tubes are equipped with defense mechanisms and once wound is inflicted, protein clogging and callose sealing are activated. However, as both mechanisms are calcium dependent [14] the presence of calcium chelating agents such as ethylenediaminetetraacetate (EDTA) or ethylene-glycol-bis-(b-aminoethyl-ether) N, N9-tetraactetate (EGTA) decreases the abundance of free Ca^{2+} in the sieve elements [10] allowing collection of phloem exudate from excised stems [9]. Hence, EDTA enables collection of phloem sap from the wound at the petiole which would otherwise be sealed as part of the plant defense mechanism.

Exudation technique is a good method of obtaining phloem sap from *Arabidopsis*. It provides an alternative to stylet-cutting techniques [15] which may pose problems in terms of finding suitable insects, collecting sufficient amount of sample for analysis and especially during cutting of stylet. Furthermore, samples from stylet-cutting technique are only obtained from sieve elements accepted and fed by the aphids [11, 13].

Table 3 The main components in palm oil [16]

Peak (cm^{-1})	Functional group
3026	Cis double bond stretching
2919	Asymmetrical and symmetrical stretching vibration of methylene (-CH$_2$) group
1743	Ester carbonyl functional group of the triglycerides
1604	Cis (-C=C-) stretching
1495	Bending vibrations of the CH$_2$ and CH$_3$ aliphatic groups
1458.45	(-CH) symmetric, CH asymmetric, CH bending stretching in organic fatty acid.
1378.83	(-C-HCCH3) bending vibrating (scissoring)
1080.97	C-O stretching
725.59	(-CH=CH-) bond pending present unsaturated fatty acid

3.2 Feasibility Assessment

For preliminary study, a quick test has been carried out on the oil samples to prove the effectiveness of quantitative method. Two standard samples were prepared (known as between standards) in which each standard was repeated three times (known as between measurements). The purpose of this test is to identify the conditions of samples whether it was more toward random noise or sample-to-sample inconsistency during resonate at a specific frequency. Table 4 shows the analysis of variance of statistical results from the feasibility assessment. The sum of square between standard and between measurements was 0.133 and 0 respectively. This indicated the amount of variation due to spectral features of samples (between standards) was sufficiently higher than the variation due to noise and sampling reproducibility (between measurements). It shows the repeated samples (between measurements) contain no noise during

absorption of radiant and constant measurement. Meanwhile, the samples with different concentration (between standard) will not overlap with absorption band of any other samples. Therefore, Simple Beer Law's method was feasible to be applied to determine the oil concentration.

Table 4 Analysis of variance

	Sum of Squares	Degree of freedom	Mean square
Between standards	0.133	1	0.133
Between measurements	0	4	0

3.3 Analysis Region

As mentioned in Section 3.1, the IR spectroscopy was used to identify specific functional groups of oil. Figure 3 shows FTIR spectrum of samples with different oil concentrations. Peak at 1495 cm^{-1} represent CH$_2$ and CH$_3$ aliphatic group bending vibrations whereas peak 1604 cm^{-1} show the results due to the existence of cis (-C=C-) stretching vibrations. Meanwhile, peaks at 1743 cm^{-1} represent triglycerides group from the analysis.
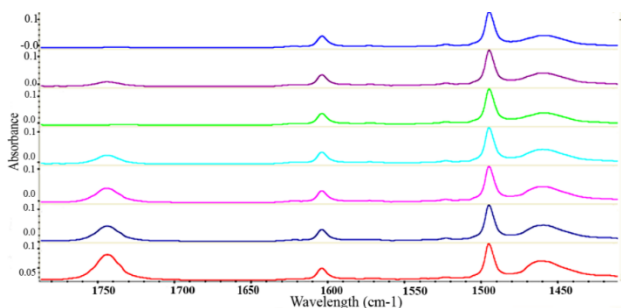

Figure 3 Transmittance spectra for standard oil solution

Figure 4 shows spectra region suggested by Simple Beer's Law for the regression analysis specifically at wavelength 2000 cm^{-1} to 1500 cm^{-1}. Three standards of samples were analysed from 0.5 wt.%, 3.0 wt.% and 6.0 wt.% of oil, respectively. TQ Analyst software interpreted high, medium and low concentration of component to display the spectra standards which was absorbed in recommended region. From Figure 4, triglycerides absorbed in the IR spectra were in the region boundaries starting from 1789.62 to 1697.53 cm^{-1}. The baseline points were set to be 1858.08 cm^{-1} and 1669.09 cm^{-1} to control the analytical region.
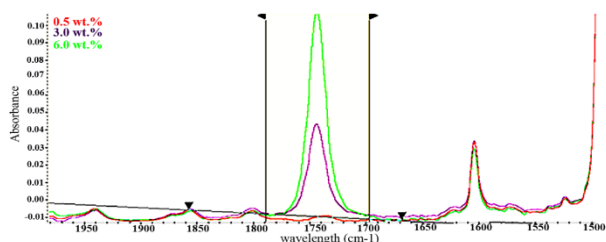

Figure 4 Recommended region for ATR-FTIR analysis

3.4 Quantitative Analysis using Simple Beer Laws

Quantification of oil contents was evaluated using Simple Beer's Law method. It stated that there is a linear relationship between the measured absorbance and the concentration of the compound of interest. The mathematical model for Beer Law's can be simply referred as the Equation [17]:

$$A = a.b.c \qquad (1)$$

where A is the measured absorbance (peak area/peak height), a is absorptivity of the samples, b is the path length and c is the sample concentration. According to Equation 1, absorbance was linearly proportional to the sample concentration where the absorptivity and path length were constant. Path length is a parameter which affects the sensitivity of the absorbance accessory. The absorbance of triglycerides for each sample was identified during scanning process and the concentration for each sample was measured using Equation 1. Therefore, the actual value of oil concentration was compared and analysed to develop a model.

The calibration curve was drawn from the standard oil solution as shown in Figure 5. The graph showed that the calibration data points fall within the concentration of 0.5 to 7.0 wt. % of oil. This straight line with a regression coefficient (R^2) of 0.99267 indicating that the actual value was almost linear within the range tested[18]. The actual value represents the dried oil residues from the drying process where else the measured value represents the measurement at area of the peak. The oil content was measured by following equation:

$$Oil\ concentration\ (wt.\%) = \frac{dried\ oil\ residue}{total\ extract\ solution}\ x\ 100 \qquad (2)$$

The linear curve can be referred to the following equations:

$$y = 0.293x \qquad (3)$$

y is the oil concentration from ATR-FTIR method and x is the mass fraction of dried oil obtain during the drying process.
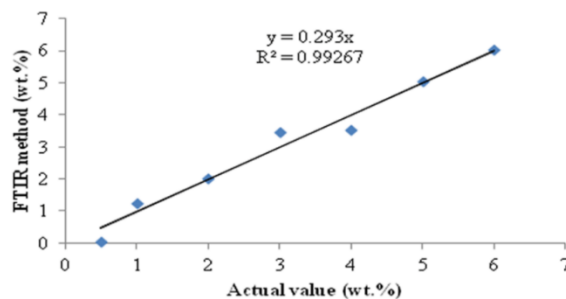

Figure 5 Calibration curve of oil concentration

3.5 Validation of Calibration for Predicting Palm Oil Samples

Figure 6 shows a linear relationship between actual value and FTIR method of oil concentration determination using ATR-FTIR. The '+' signs represent the standard oil concentration from the permeated water, which were the standard solutions for validation purpose. The correlation between actual value and FTIR method was high, the R^2 value was 0.9913 which nearly to

1. The RMSEP value for validation was 0.00831. From the results obtained, this indicates there is no overfitting between actual value and FTIR method because the high values of R^2 in calibration curve. Moreover, this was followed by high value of R^2 in validation curve. It means the validation data falls within the calibration line.
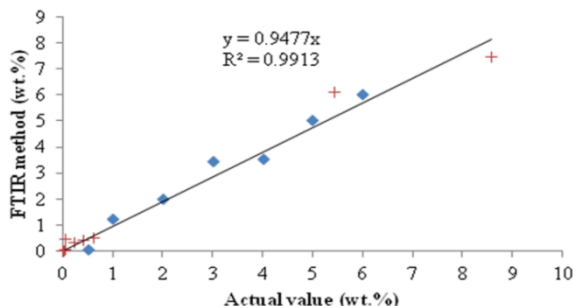

Figure 6 Validation of curve using permeated water samples

Table 5 shows the permeate concentration and rejection of UF membrane from oil emulsion. The feed stream with 85.6 wt.% of oil content was reduced to 61.4 wt.% of oil after UF treatment in FTIR method. Meanwhile, turbidity methods of the feed stream at 85.6 wt.% of oil shows 70300 NTU suspended solid in the samples solution and reduced drastically to 27 NTU. For second run, 54.3 wt.% of oil in feed stream decreased to 4.11 wt.% of oil after UF treatment using FTIR method and for turbidity method, the oil concentration decreased from 32700 NTU to 13 NTU. Oil concentration from feed stream of 21.8 wt.% decreased to 0.53 wt.% after filtered. Turbidity method indicates that the oil was reduced from 4850 NTU to <0.01 NTU. The trends were similar for other samples which were summarized in Table 5.

Table 5 Concentration of oil content after filtration process

Initial oil concentration from FTIR (wt%)	Final concentration from FTIR (wt.%)	oil Initial from turbidity (NTU)	Final turbidity (NTU)
85.6	6.14	70300	27
54.3	4.11	32700	13
2.18	0.53	4850	< 0.01
0.46	0.19	35.8	< 0.01
0.06	0.01	33.5	< 0.01

From the above finding, ATR-FTIR was the favorable method to determine the oil concentration in oil emulsion compared to turbidity method. It can be used without limitation of concentrations. Instead of measuring oil concentration, ATR-FTIR were also able to quantify the chemical components in the permeated water. Meanwhile, turbidity method can only be measured until less than 0.1 NTU. But yet, the efficiency was still low since we could not identify miniature chemical componets in the permeated water. Theoretically, the concept of turbidity was to observe particles suspension on the samples when the light was emitted. There are several disadvantages of using turbidity method. Firstly, the samples have to be diluted for higher concentration of oil. Secondly, it could not measure the oil content at low concentration. Thus, the reliability to determine the oil concentration using turbidity method can be questioned.

Therefore, the ATR-FTIR method can be used as suitable method to measure the oil content in the permeated water.

■4.0 CONCLUSION

Based on the above findings, it can be concluded that the oil concentration can be quantified using ATR-FTIR method at wavelength between 1789.62 and 1697.53 cm^{-1}. The analytical method is a non-destructive and can be used to collect data from a minimal amount of solution. Therefore, it is a favorable method compared to turbidity method.

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