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# SYNTHESIS AND CHARACTERIZATION OF MOLECULARLY IMPRINTED POLYMER IN OLEIC ACID ISOLATION FROM PALM FATTY ACID DISTILLATE WASTES

## (Sintesis dan Ciri-Ciri Polimer Tercetak Molekul dalam Pengasingan Asid Oleik Daripada Sisa Penyulingan Asid Lemak Kelapa Sawit)

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**Abstract**

In this study, molecularly imprinted polymer-oleic acid (MIPOA) was synthesized using oleic acid (OA) as the template via bulk polymerization. The objective of this study was to characterize the MIPOA as an adsorbent for the isolation of OA from palm fatty acid distillate (PFAD) waste, using thermogravimetric analysis (TGA) and Brunauer-Emmett-Teller (BET) analysis. Isolation method of OA from PFAD waste using MIPOA via esterification reaction in methanol and detection of OA by using gas chromatography–mass spectrometry (GC-MS) showed that MIPOA was capable of isolating OA from PFAD waste sample at 99.99% of isolation efficiency. Findings obtained from TGA results showed that MIPOA was less thermally-stable compared to NIP at higher temperature as the percentage weight loss of MIPOA was higher than NIP. At 215 °C, the weight loss of MIPOA (9.36%) was higher compared to NIP (6.55%) as a control due to the less branch of cross-linked polymer was successfully synthesized. Higher surface area in MIPOA compared to NIP was successfully proven in this experiment. In addition, the presence of OA as a template leaves the cavities during MIPOA washing contributes to the increase of the surface contact. Due to its high surface area and ease of degradation by external energy from heating when compared to NIP (which act as control), MIPOA has a high porosity and an abundance of an organic cross-linkage network. From BET analysis, surface area of MIPOA was 390.52 m$^2$/g and this value was relatively high in isolation efficiency for the isolation of OA methyl ester. MIPOA displays type I isotherms which indicates that the MIPOA was microporous. These results proved that MIPOA can be employed as a potential adsorbent to isolate OA from PFAD waste.

**Keywords:** molecularly imprinted polymer, oleic acid, palm fatty acid distillate

**Abstrak**

Dalam kajian ini, polimer tercetak molekul-asid oleik (MIPOA) telah disintesis menggunakan asid oleik (OA) sebagai templat melalui pempolimeran pukal. Objektif kajian ini adalah untuk mencirikan MIPOA sebagai bahan penjerap untuk mengasingkan OA daripada sisa penyulingan asid lemak sawit (PFAD), analisis termogravimetrik (TGA) dan analisis Brunauer-Emmett-Teller (BET). Kaedah pengasingan OA daripada sisa PFAD menggunakan MIPOA melalui tindak balas pengesteran dalam metanol dan pengesanan OA menggunakan kromatografi gas–jisim spektrometer (GC-MS) yang menunjukkan MIPOA mampu mengasingkan

OA daripada sampel sisa PFAD pada 99.99% kecekapan pengasingan. Dapatan diperolehi daripada keputusan TGA menunjukkan MIPOA kurang stabil dari segi haba berbanding NIP pada suhu yang lebih tinggi kerana peratusan kehilangan berat MIPOA adalah lebih tinggi daripada NIP. Pada suhu 215 °C, penurunan berat MIPOA (9.36%) adalah lebih tinggi berbanding NIP (6.55%) kerana kurang bilangan cabang polimer bersilang yang telah berjaya disintesiskan. Luas permukaan yang lebih tinggi dalam MIPOA berbanding NIP telah berjaya dibuktikan dalam eksperimen ini. Di samping itu, kehadiran OA sebagai templat dikeluarkan daripada liang kaviti semasa pencucian MIPOA menyumbang kepada peningkatan permukaan sentuhan. Oleh kerana luas permukaannya yang tinggi dan kemudahan degradasi oleh tenaga luaran daripada pemanasan jika dibandingkan dengan NIP (yang bertindak sebagai kawalan), MIPOA mempunyai keliangan yang tinggi dan kelimpahan rangkaian rantai silang organik. Daripada analisis BET, luas permukaan MIPOA ialah 390.52 m$^2$/g dan nilai ini agak tinggi dalam kecekapan pengasingan untuk pengasingan OA metil ester. Isoterma jenis paparan MIPOA I yang menunjukkan bahawa MIPOA adalah mikroliang. Keputusan ini membuktikan bahawa MIPOA boleh digunakan sebagai penjerap yang berpotensi untuk mengasingkan OA daripada sisa PFAD.

**Kata kunci:** Polimer tercetak molekul, asid oleik, sulingan asid lemak sawit

## Introduction

Palm Fatty Acid Distillate (PFAD) is a processing residue resulting from the physical refining of crude palm oil (CPO) products. The annual global production of PFAD is estimated at $2.5 \times 10^6$ tons, where Malaysia (29%) and Indonesia (58%) are the main contributors [1]. PFAD consists of more than 80% of free fatty acids, primarily palmitic acid, and oleic acid, which can be esterified and added to the biofuel and oleo-chemical industries as feedstock. Free fatty acid (FFA) is an important specification that influences the palm oil quality. According to previous study, PFAD contains roughly 40% of oleic acid (Figure 1), depending on the quality of CPO. Oleic acid (OA) is the most abundant monounsaturated fatty acid in nature which plays important roles in many industries. OA has multiple properties and applications of great value and importance. OA has been used in a variety of industries and sectors that produce many products such as textiles, cosmetics, inks, paints, pharmaceuticals, detergents, and food processing.
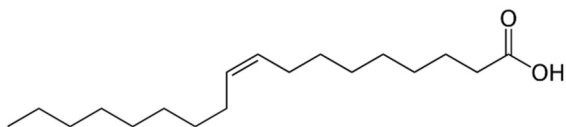


Figure 1. Molecular structure of OA

Throughout the years, different kinds of sorbents were developed to isolate variety of free fatty acids from PFAD waste. Molecularly imprinted polymer (MIP) is one of the sorbents used in research and development which shows great findings. MIP is a synthetic polymer with a predetermined selectivity for a given analyte, or group of structurally related compounds, making them ideal materials to be used in separation processes [2]. For the synthesis of MIP, relevant selection of the template, monomer, crosslinker, and porogen solvent is considered critical to produce high percentage of analyte isolation.

MIPs offer many advantageous features such as simple to synthesize and easy to prepare [3], low cost, and can maintain its performance even if it is stored for several years. They are intrinsically more stable chemically and physically, and robust due to their highly cross-linked polymer nature, which facilitates their application in harsh environments such as in the presence of strong acids or bases, organic solvents, and high temperature and pressures [4]. In this study, the use of MIP as isolation technique of OA from PFAD waste has been proposed to obtain OA from the PFAD waste. The synthesized MIP for oleic acid has been characterized via esterification reaction in methanol with gas chromatography–mass spectrometry (GC-MS), TGA, and BET analysis.

## Materials and Methods

### Synthesis of MIPOA

The MIP was prepared by following Kugimiya's synthesis method [5]. All ingredients (1.0 mmol oleic acid, 4.0 mmol of allylthiourea, 20 mmol of EGDMA, and 0.12 mmol of AIBN initiators) were dissolved in 4.0 mL of acetonitrile. The solution was then sonicated and purged with nitrogen gas for 5 minutes to remove oxygen gas from the solution. Then, the sealed solution was polymerized at 60 °C in a water bath for 24 hours.

The resulting polymer was washed with methanol/acetic acid (9:1, v/v) using a Soxhlet apparatus to remove oleic acid template. A final washing step using 25 mL of methanol for 3 times washing was carried out and a polymer was centrifuged at 5300 rpm for 3 mins to remove residual of acetic acid. The supernatant methanol was analyzed using a UV spectrophotometer at 280 nm to confirm that there was no OA remains in the cross-linked polymer. Afterwards, the polymer was dried at 60 °C under vacuum overnight and stored at room temperature. Finally, the polymer was ground using mortar and pestle, and sieved to yield particle size between 28 μm and 100 μm. The non-imprinted polymer (NIP) as a control was synthesized using the same procedure described above, with the absence of OA, to evaluate the sorption capacity of the polymer itself and to discriminate from the adsorption of the selective sites of MIP [3].

**MIPOA characteristics**
**Isolation of OA from PFAD waste**
The PFAD sample was turned into liquid form at room temperature by esterification process which changed it to fatty acid methyl esters (FAME) [6][7]. Esterification of PFAD was conducted in a flask equipped with reflux condenser and temperature indicator on a hot plate with a magnetic stirrer shown in Figure 2. The mixture of methanol and PFAD was heated to 60ºC under continuous stirring at 500 rpm. The experiment was carried out at around 60ºC-80ºC for a few hours. The

volume ratio of methanol to PFAD used was 2:1. The mixture was then separated into six different small jars and left at room temperature. Next, 20 mg of MIPOA and NIP were added and stirred for 1 hour into the mixture solution, respectively (Figure 3). The experiment was carried out in duplicate. After that, the oil-based mixture solution was collected for detection of OA using GC-MS.
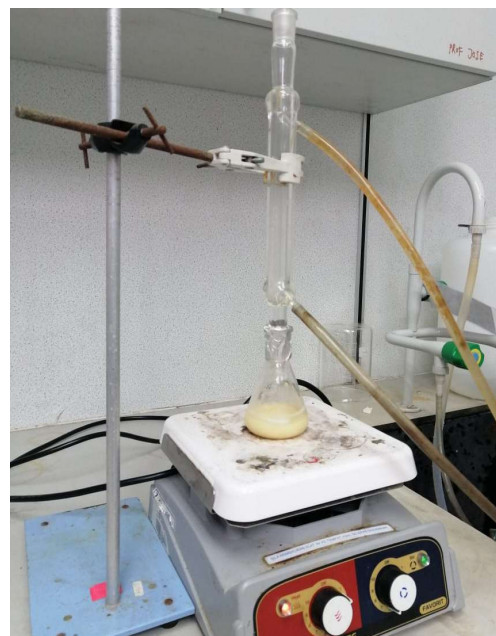


Figure 2. Esterification reaction set-up experiment using PFAD sample
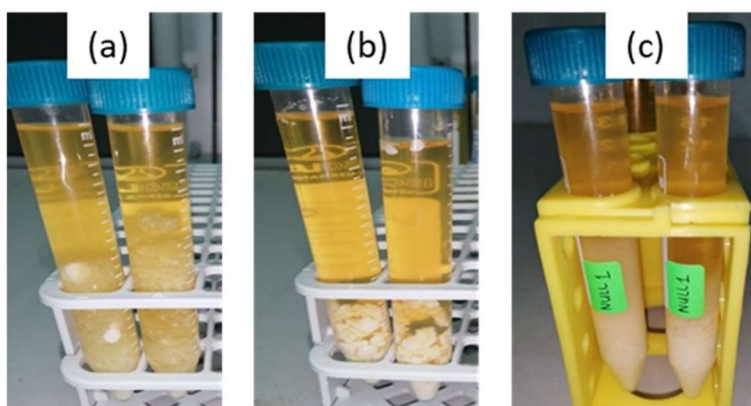


Figure 3. Oil-based mixtures were seen to accumulate solids in different form of yield at room temperature (a) PFAD-methanol after mixed with MIPOA (b) PFAD-methanol after mixed with NIP as a control and (c) PFAD-methanol with absence of any adsorbent.

An Agilent 7890A gas chromatography equipped with a BPX5 capillary column size 30 m × 0.25 mm i.d. (0.25 µm stationary film thickness) was used with helium (purity 99.999%) as carrier gas at a flow rate of 1.2 mL $min^{-1}$. The initial oven temperature was held at 50 °C for 1 min, and then increased to 280 °C at 20 °C $min^{-1}$, and held at 280 °C for 1 min. The total analysis run time was 13.5 minutes. The injector temperature was set at 280 °C, and the injection was performed in the splitless mode. The identification of analyte was done by GC retention time ($R_t$) and by a comparison of the mass spectra of identified substances with those of authentic reference substances.

**TGA Analysis of MIPOA**
The thermal degradation of different samples for non-isothermal conditions was investigated thermogravimetrically. The calculation of kinetic parameters was carried out under a heating rate of 30 °C $min^{-1}$ in 30-700 °C using a thermogravimetric analyzer (TGA) instrument (model STA7200). In order to minimize the test error, the weight of all the samples in powder form (177 < 210 mm) was identical to be 6 mg to 7 mg. The TGA experiments was carried out in a

nitrogen atmosphere (99.99% minimum purity) with a flow rate of 30 mL $min^{-1}$ [8].

**BET analysis of MIPOA**
In order to determine the MIPOA surface area, an automated gas adsorption analyzer model ASAP2020 (Micromeritics Instrument Corporation, USA) was used with adsorption-desorption isotherms of nitrogen gas temperature sets at -195.89 °C. About 0.05g of sample was used for each analysis. The samples were automatically degassed at 22 °C under nitrogen for at least 24 hours. The specific surface areas of sample were calculated by the BET (Brunauer, Emmett, and Teller) method, while volume of micropore was estimated using the Dubinin Radushkevich (DR) equation. For pore volume, it was directly calculated from the volume of nitrogen held at the highest relative pressure (P/Pᵒ = 0.99).

**Results and Discussion**
**Ability of MIPOA to isolate OA from PFAD waste**
Standard solution was Chromatogram of OA standard shows that the $R_t$ for OA occurs at 11.73 mins as a main peak (Figure 4).
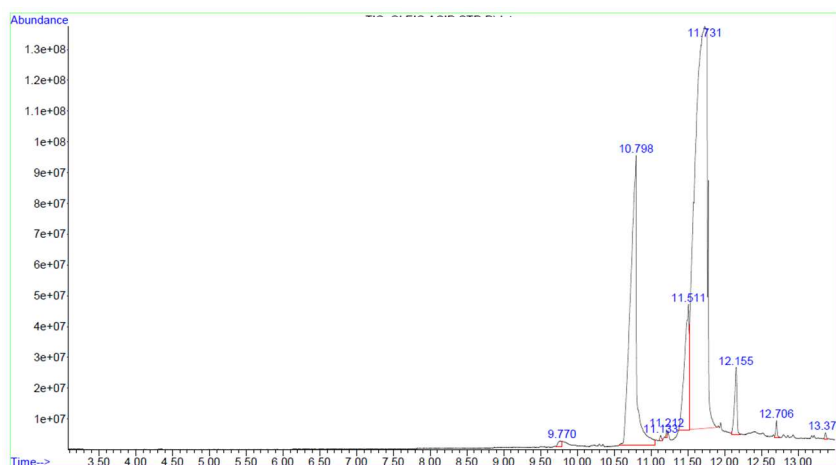


Figure 4. Chromatogram for OA standard using GC-MS

Figure 5 shows the GC-MS chromatogram of the untreated PFAD sample after esterification to produce methyl ester compounds from various free fatty acids. In a PFAD sample with a volume ratio of 1:2 between PFAD and methanol, the composition of certain

prominent peaks produced by esterification of free fatty acids is as displayed in Table 1. The fragmentation pattern of the major active compound ($R_t$ = 10.8 mins) was determined as n-Hexadecanoic acid methyl ester or methyl palmitate. OA methyl ester or methyl oleate was

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found to be the second higher abundance at the $R_t$ equals to 11.7 mins. Therefore, detection of OA in treated PFAD samples with MIPOA and NIP was observed at $R_t$ around 11.7 mins as mentioned in calibration of OA standard. There was a possibility of peak overlapping occurred at 11.7 mins. However, for the recent findings, it was estimated that OA methyl ester was observed at 11.7 mins by referring to the chromatograms obtained.
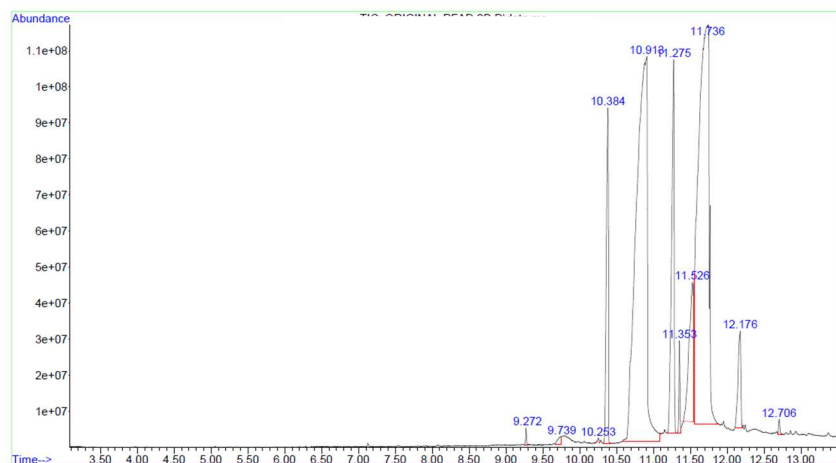


Figure 5. GC-MS chromatogram of PFAD sample in methanol with volume ratio of PFAD to methanol equals to 1:2 with absence of any adsorbent

Table 1. Some major peaks found in untreated PFAD sample

| Peak | Retention time, $R_t$ | % Composition | Compound |
|---|---|---|---|
| 1 | 9.2724 | 0.14 | Tridecanoic acid methyl ester |
| 2 | 9.7389 | 0.23 | Tetradecanoic acid |
| 3 | 10.2526 | 0.06 | Cyclopentadecanone methyl ester |
| 4 | 10.9131 | 38.28 | n-Hexadecanoic acid methyl ester/ palmitic acid methyl ester |
| 5 | 11.2748 | 8.42 | 9-Octadecenoic acid methyl ester |
| 6 | 11.3534 | 0.83 | Octadecanoic acid methyl ester |
| 7 | 11.7361 | 38.19 | Oleic acid methyl ester |

Figure 6 displays the GC-MS chromatogram of treated PFAD sample with MIPOA in methanol. From the results, OA methyl ester was totally isolated with composition left about 0.03% contained in the free oil-based mixture. Palmitic acid methyl ester was not isolated at all as even palmitic acid methyl ester contained about 38.28% in the PFAD samples. The composition of palmitic acid methyl ester was higher after being treated with MIPOA due to the potential of stirring and heating process which caused the increasing in oil viscosity. It was proved that MIPOA was highly selective for the isolation of OA methyl ester. Palmitic acid methyl ester was not isolated at all after being treated with MIPOA. In Table 2, the composition analysis from the chromatogram showed significant peaks of compound present in PFAD samples treated with MIPOA. There was possibility at 11.7 mins that the redundant peaks were determined. However, further study is required to enhance the separation peaks at approximately 11.6 mins until 11.7 mins to identify the ghost peak which was redundant with OA methyl ester peak in the chromatogram.
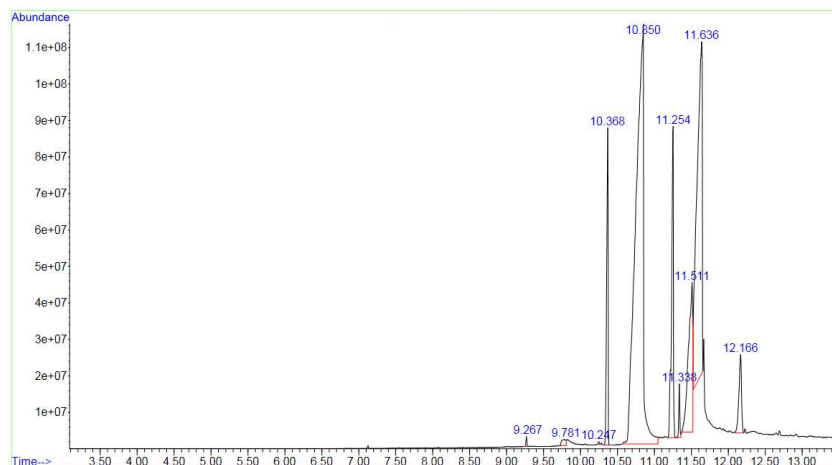
Figure 6. GC-MS chromatogram of PFAD sample after treated with MIPOA as an adsorbent in methanol with volume ratio of PFAD to methanol equals to 1:2.

Table 2. GC-MS analysis in PFAD sample after treated with MIPOA as an adsorbent in methanol

| Peak | Retention time, $R_t$ | % Composition | Compound |
|---|---|---|---|
| 1 | 9.2671 | 0.1361 | Tridecanoic acid methyl ester |
| 2 | 9.7808 | 0.4017 | Tetradecanoic acid |
| 3 | 10.8502 | 46.8937 | n-Hexadecanoic acid methyl ester |
| 4 | 11.2538 | 8.0424 | 9-Octadecenoic acid methyl ester |
| 5 | 11.3377 | 0.7857 | Octadecanoic acid methyl ester |
| 6 | 11.5107 | 9.2846 | Linoleic Acid methyl ester |
| 7 | 11.7361 | 0.0300 | Oleic acid methyl ester |

GC-MS chromatograms of treated PFAD samples with NIP as a control is shown in Figure 7 whereas the significant peaks of compounds present in PFAD samples treated with NIP is shown in Table 3. From the results, at $R_t$ equals to 11.71 mins, the peak for OA methyl ester was presented with composition at 34.53% in free oil-based mixture. The same trend was found when PFAD sample was treated with NIP. The abundance of OA methyl ester was found to be higher compared to the initial condition.
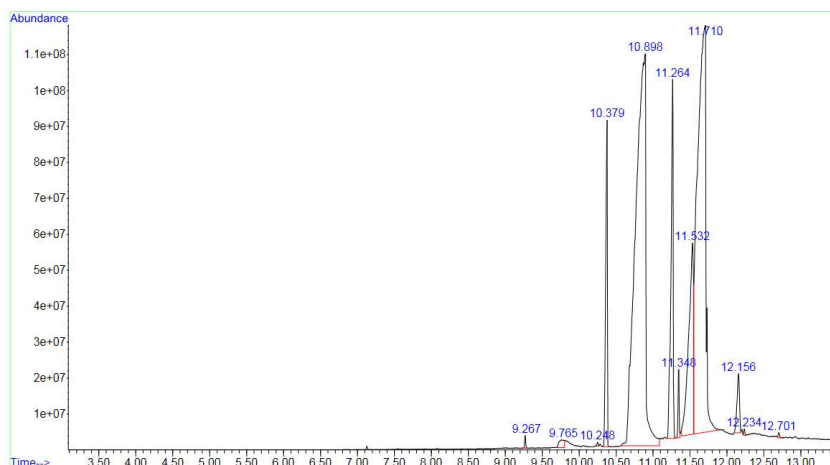
Figure 7. GC-MS chromatogram of PFAD sample after treated with NIP as an adsorbent in methanol with volume ratio of PFAD to methanol equals to 1:2

Table 3. GC-MS analysis in PFAD sample after treated with NIP as an adsorbent in methanol

| Peak | Retention time, $R_t$ | % Composition | Compound |
|------|------------------------|----------------|----------|
| 1 | 9.2673 | 0.128 | Tridecanoic acid, 12-methyl-, methyl ester |
| 2 | 9.7653 | 0.4011 | Tetradecanoic acid |
| 3 | 10.8975 | 40.1635 | n-Hexadecanoic acid methyl ester |
| 4 | 11.2645 | 7.7556 | 8-Octadecenoic acid, methyl ester |
| 5 | 11.3483 | 0.7522 | Octadecanoic acid, methyl ester |
| 6 | 11.7100 | 34.5268 | Oleic Acid methyl ester |

The OA methyl ester found at $R_t$ around 11.7 mins in treated sample with MIPOA and NIP respectively are shown in Table 4. The average percentage of oleic acid adsorbed by MIPOA at $R_t$ around 11.7 mins is 99.99%, while the adsorption by NIP samples is 0.88%. This result shows that MIP was capable of isolating oleic acid from PFAD sample. The differences of oleic acid adsorbed by MIPOA and NIP samples are not that high, probably due to some of the template on MIP vanished during crushing and the medium of sample is in oil-based which makes it difficult for MIP to extract because of its high viscosity properties. In addition, using real sample commonly contributes to the unknown compound which is present in the samples due to the matrix effect.

Table 4. % OA methyl ester adsorbed by MIPOA and NIP

| Composition of OA methyl ester | MIPOA | NIP |
|---|---|---|
| % Initial composition | 38.190 | 38.190 |
| % Final composition | 0.002 | 38.526 |
| % Adsorbed | 99.99 | 0.88 |

**BET analysis**
**Isotherm linear plot (BET)- $N^2$ adsorption isotherm in MIPOA**

The $N^2$ adsorption isotherms of the MIPOA is shown in Figure 8. From this figure, MIPOA displays type I isotherms and according to International Union of Pure

and Applied Chemistry (IUPAC) classification, it indicates that the MIPOA is microporous. Usually, Type I isotherm displays a convex curve, and the platform of this type comes out horizontal or virtually horizontal, and the adsorption isotherm directly intersects with the line $P/P^o = 1$ [9]. As seen in the initial stage, the volume adsorbed increased sharply at low relative pressure region ($P/P^o < 0.2$). This means that nitrogen molecules were adsorbed mainly in the microporous structure [9]. Table 5 presents the BET surface area, total pore volume, micropore volume, and average pore diameter of MIPOA that were obtained from $N^2$ adsorption isotherms. The surface area of MIPOA was 390.52 $m^2/g$ and this value was considered to have potential in adsorbing OA at high isolation efficiency.
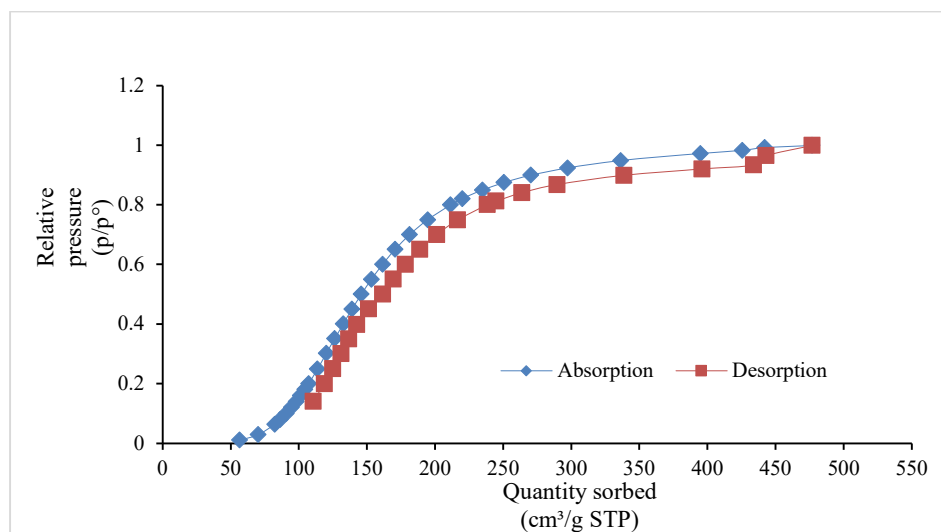


Figure 8. $N_2$ gas adsorption-desorption isotherms of MIPOA

Table 5. BET surface area, total pore volume, micropore volume and average pore diameter of MIPOA

| Sample | BET Surface Area ($m^2/g$) | Total Pore Volume ($cm^3/g$) | Micropore Volume ($cm^3/g$) | Average Pore Diameter (Å) |
|---|---|---|---|---|
| MIPOA | 390.52 | 0.6106 | 0.0072 | 62.55 |

**TGA analysis**

During a ramped heating under nitrogen, such as in a TGA experiment, the degradation process usually passes through three stages. In the first and second stage, the less branch cross-linked bonds located at the outer side of the particles were decomposed. Whereas more stable structure polymer which consists of substituted allylthiourea as an active site was degraded in the third stage due to the inner part of the polymer particles contributing to the stability of MIPOA. The final step was the high temperature degradation of these stabilised structures to yield volatile products and a small quantity of carbonaceous char.

The curves for MIPOA display three weight loss stages (DTG maxima at 215 °C, 390 °C and 450 °C) that lead to the formation of a small high temperature residue (9.36 wt.%) (Figure 9). The first DTG peak can be related to the overlapping of less branch of polymer chain (degradation) and char-forming secondary reactions (cross-linking), whereas the second peak corresponds to decomposition of the stabilised allylthiourea structures. The similar temperature range was observed for NIP as a control which led to the formation of a small high temperature residue (6.55 wt.%) (Figure 10).
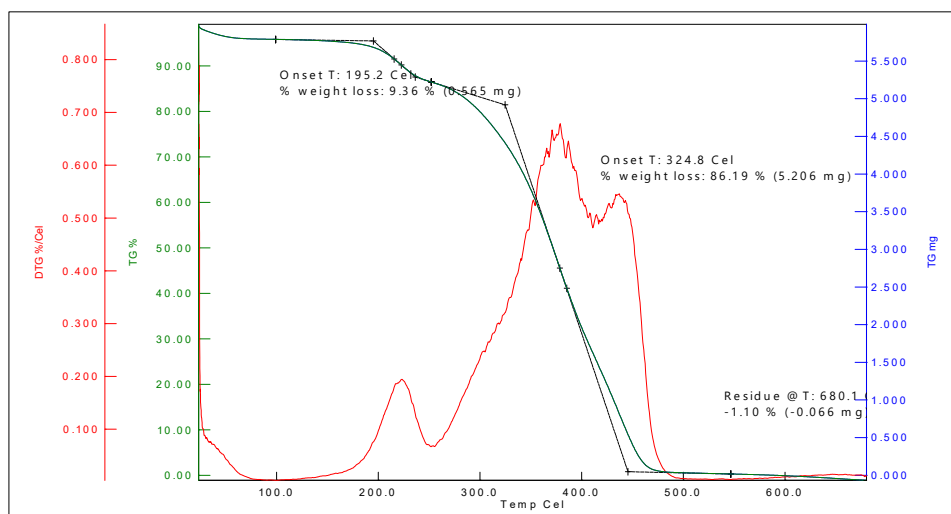
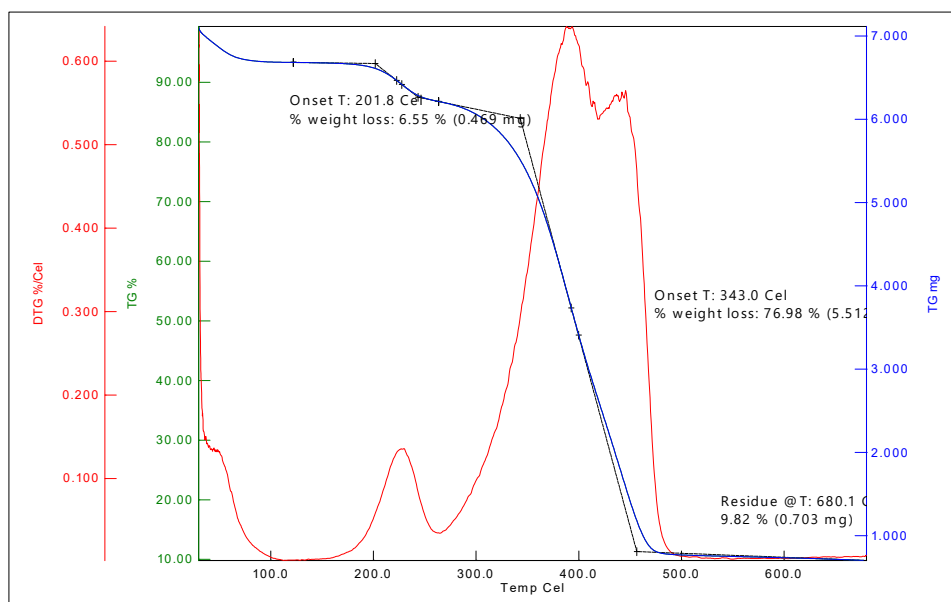Figure 9. TGA thermogram of MIPOA before isolation



Figure 10. TGA thermogram of NIP as a control

From Table 6, the weight loss due to the degradation was investigated. At 215 °C, the weight loss of MIPOA (9.36%) was higher compared to NIP (6.55%) as a control due to the less branch of cross-linked polymer which was successfully synthesized. Higher surface area in MIPOA compared to NIP was successfully proven in this experiment. In addition, the presence of OA as a template leaves the cavities during MIPOA washing contributes to the increase of the surface contact. At 330 °C, MIPOA (86.19%) also showed higher mass loss compared to NIP (76.98%). In the synthesis of polymer, the cross-linked effect gives benefits in terms of affinity properties as a sorbent and higher surface area of MIPOA.

Table 6. Percentage weight loss of MIPOA and NIP within temperature range of 0 ºC to 400 ºC

| DTG Temperature (ºC) | MIPOA (% weight loss) | NIP (% weight loss) |
|---|---|---|
| 215 | 9.36 | 6.55 |
| 330 | 86.19 | 76.98 |
| 680 | 0.00 | 9.82 |

## Conclusion

In this research, MIPOA was successfully synthesized using oleic acid as template, acetonitrile as a porogen solvent, allylthiourea as functional monomer, and EGDMA as a cross-linker. Both MIPOA and NIP were synthesized by bulk polymerization technique. The synthesized MIPOA and NIP were successfully characterized by using GC-MS, TGA and BET instruments to understand its sorption ability and thermal properties. Based on GC-MS analysis, the average percentage of oleic acid adsorbed by MIPOA samples at $R_t$ around 11.7 is 99.99%, while by NIP samples is 0.88%. This proves that MIPOA was capable of isolating OA from PFAD sample. BET analysis shows that MIPOA displays type I isotherms and indicates that the MIPOA was microporous. Lastly, TGA data shows that MIPOA was less thermally-stable compared to NIP at higher temperature due to high surface area. The higher % weight loss of MIPOA than NIP ensured the presence of an organic cross-linked network. This study concludes that MIPOA was successfully employed for the effective and selective isolation of oleic acid from PFAD waste.

## Acknowledgement

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