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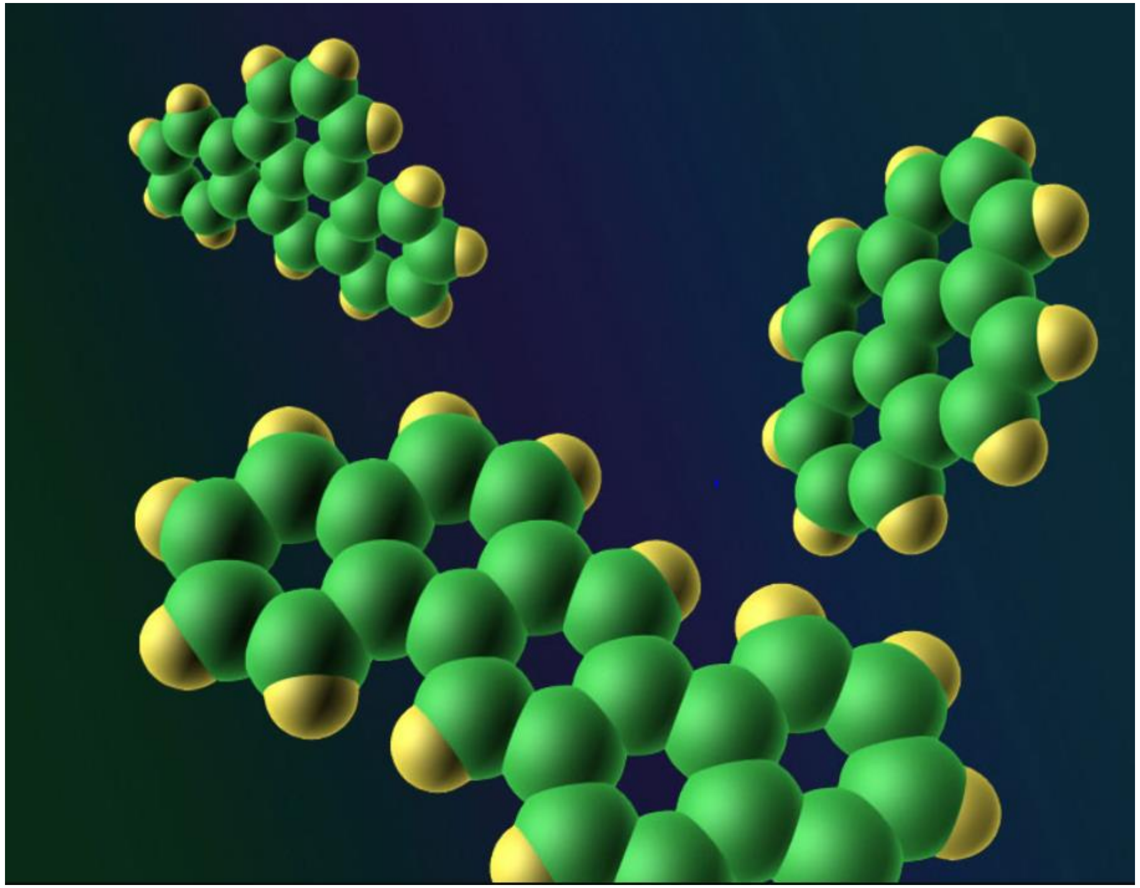
Comparison of Different Sorption Media and Removal Efficiency on Polycyclic Aromatic Hydrocarbons (PAH) in Palm Oil

Gibson Yao Sheng Tan, Dr Jibrail Kansedo, Dr Yie Hua Tan

Introduction

- Polycyclic aromatic hydrocarbons (PAHs) are primarily formed from the incomplete combustion of organic matter. As a result, they are widely distributed in the environment.

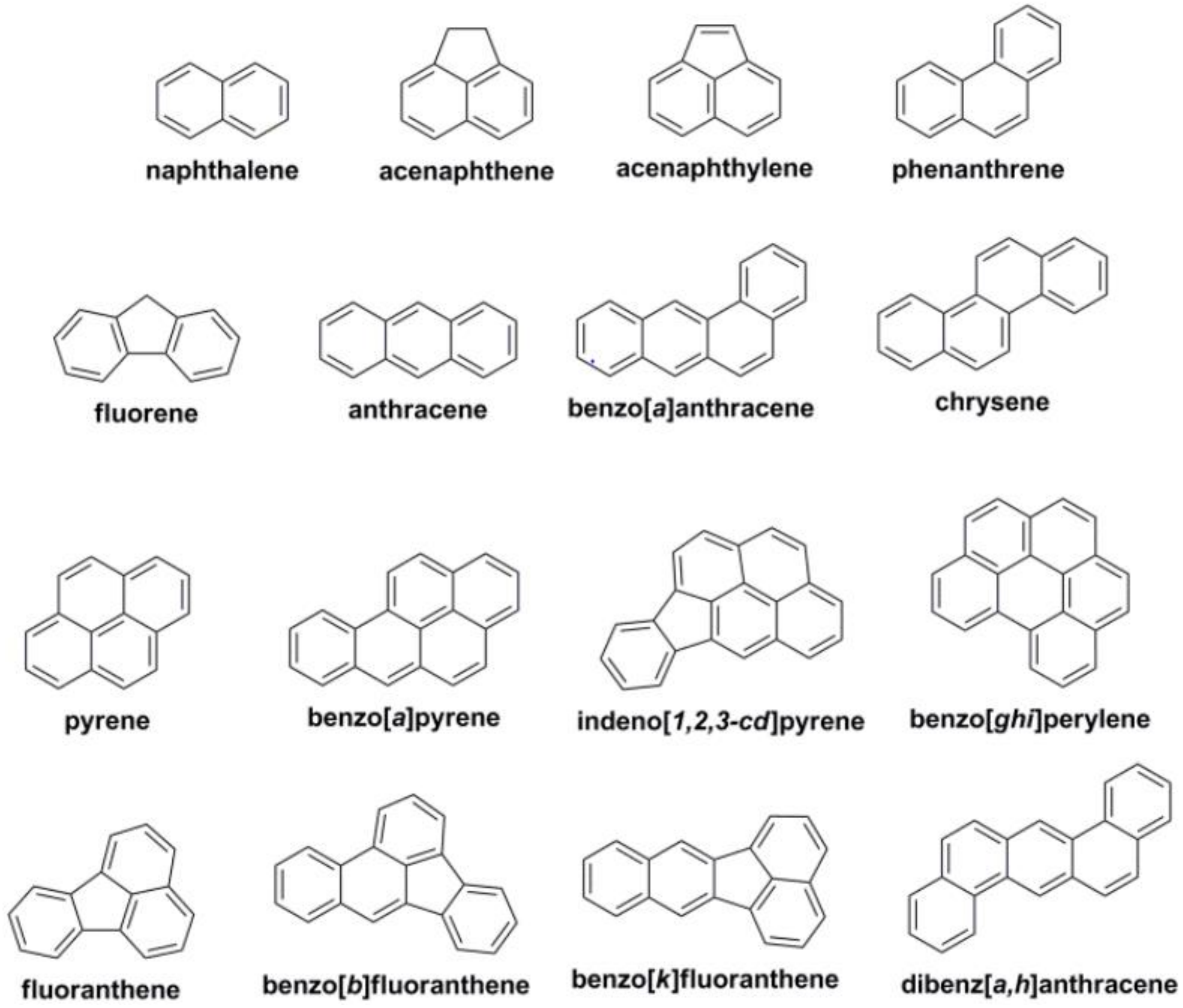
- PAHs and their epoxides are highly mutagenic towards living organisms which includes human beings.



What are PAHs?

- PAHs are organic compounds containing primarily only carbon and hydrogen which are composed of multiple aromatic rings. The electrons in these organic rings are highly delocalized (Ahad 2015).

- The United States Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) have categorized 16 PAHs out of the hundred other different types as part of the priority list due to their xenobiotic effects presented to human health and the environment (Abdel 2016).



Sources and Routes of Contamination of PAHs

- Research towards PAHs initially began from the environmental field where industrial sources of PAHs were primary targets of analysis. However, with the increment of anthropogenic activities, these pollutants are gradually increasing and are capable of migrating from its environment into vegetable crops, food and especially edible oils.
- According to (Phillip 1999), 70% of PAH exposure for non-smokers are primarily attributed to dietary intake, causing food to possess the largest impacts towards non occupational exposure of PAHs.

Literature Review

- PAHs in edible oil are commonly removed via adsorbents (bentonite clay) during the degumming and bleaching process, leaving only trace amounts which should meet the legal limits for safe consumption set by the country.
- However, according to studies conducted by Fakhri (2018) and Sekeroglu, Gogus and Fadiloglu (2007), edible oils in the current markets are showing signs of no longer meeting the legal limits of PAHs content set by their respective countries and this trend would continue to persist with the continuous increment of anthropogenic activities.
- Hence, the need of alternative adsorbents that are more effective in terms of PAH removal are required in order to effectively reduce the PAH levels to a safe level of consumption. Activated carbons especially bamboo activated carbon has shown to be extremely effective towards impurities in various adsorption applications, however up to date there has yet to be studies conducted that focuses on the removal of PAHs from edible oils.

Literature Review

Table 1 : Legal Limits and Regulations for Food Worldwide (Sun, Wu, and Gong 2019)

Product	*Benzo[a]Pyrene µg/kg*	*Sum of PAH4 µg/kg*
European Union		
Oils and fats (excluding cocoa butter and coconut oil) intended for direct human consumption or use as an ingredient in food	***2.0***	***10.0***
China		
Grain (Brown rice, rice, wheat, wheat flour, corn, cornmeal)	***5.0***	–
Meat products (Smoked, roasted, grilled meat products)	***5.0***	–
Aquatic products (Smoked, roasted aquatic products)	***5.0***	–
Fats and oils	***10.0***	–

Methodology

Step 1: Preparation of Activated Carbon

Bamboo charcoal was purchased from the local market and is then washed, dried and activated with activating agents to produce bamboo waste activated carbon.

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Step 2: Sample Preparation Phase

The refined palm oil is mixed together with Benzo[a]pyrene (BaP) which was purchased from Sigma Aldrich to produce synthetic oil with a PAH concentration of 2g/L

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Step 3: Analytical Phase

The activated carbon and industrial bleaching earths are mixed with the synthetic oil to remove the PAHs. The sample is then diluted with pyridine before analysing with GCMS.

- **BaP which is known as a global PAH indicator is primarily selected for the experimental work conducted.**
- **Activating agents used for the activating process of the bamboo charcoal were sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH)**
- **Pyridine acts as the main solvent for the sample and is diluted with a dilution factor of 20.**
- **Removal efficiencies of PAHs for each respective adsorbent is analysed using GCMS.**

Methodology

Settings for GCMS for the Analysis of PAHs Content in Refined Palm Oil

Oven Ramp	°C/min	Next ° C	Holding Time (min)	Run Time (min)
Initial		50	1	1
Ramp 1	8	150	5	18.50
Ramp 2	5	200	5	33.50
Ramp 3	5	280	5	54.50
Post Run	-	50	0	54.50

Gas Flowrate : 1mL/min

Column : Model No: Agilent 19091S-433
HP-5MS 5% Phenyl Methyl Siloxane
Capillary 30 m x 250um x 0.25 um nominal

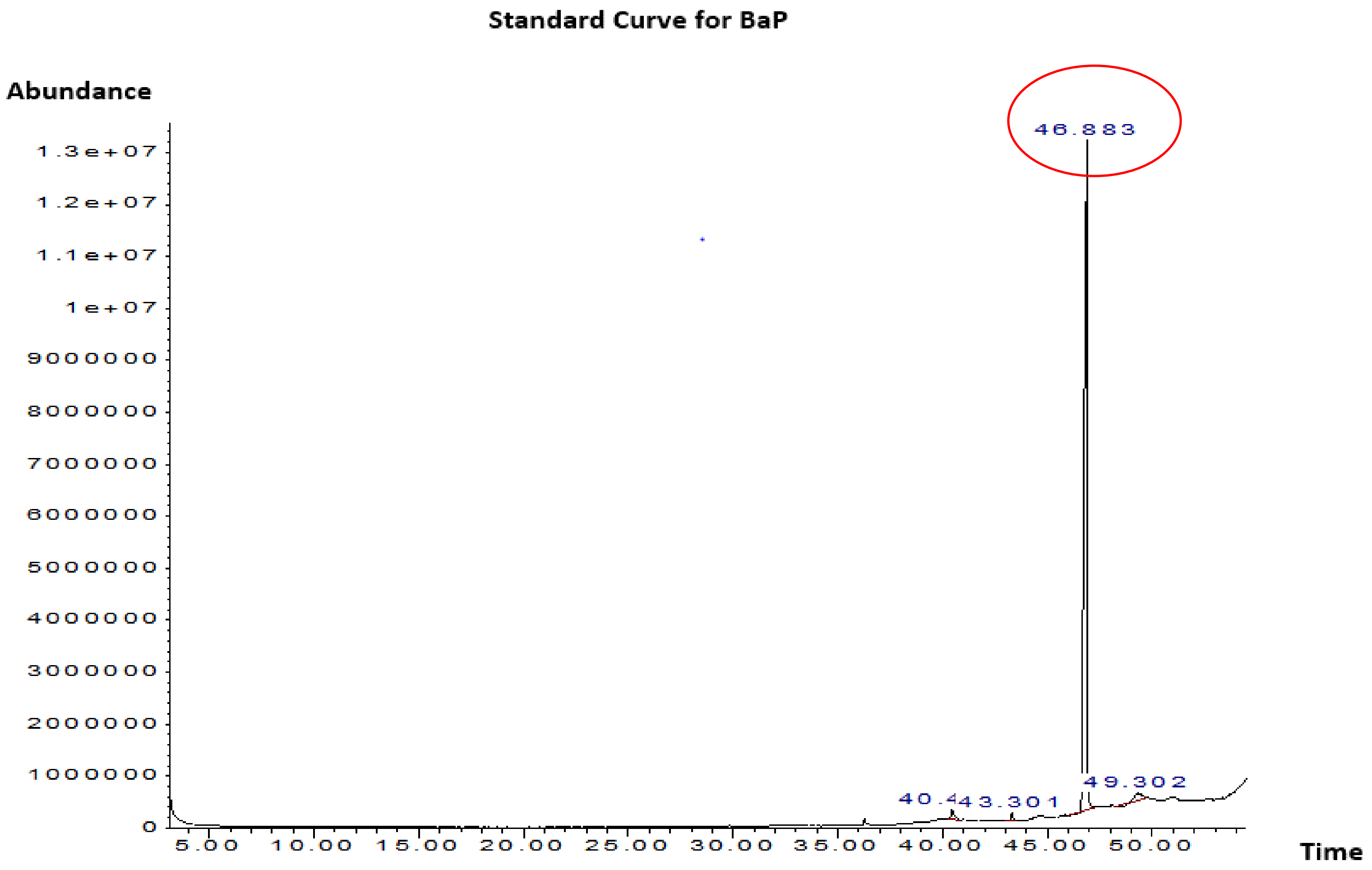
Split Ratio : 20

Dilution Factor : 20

Solvent Used : Pyridine

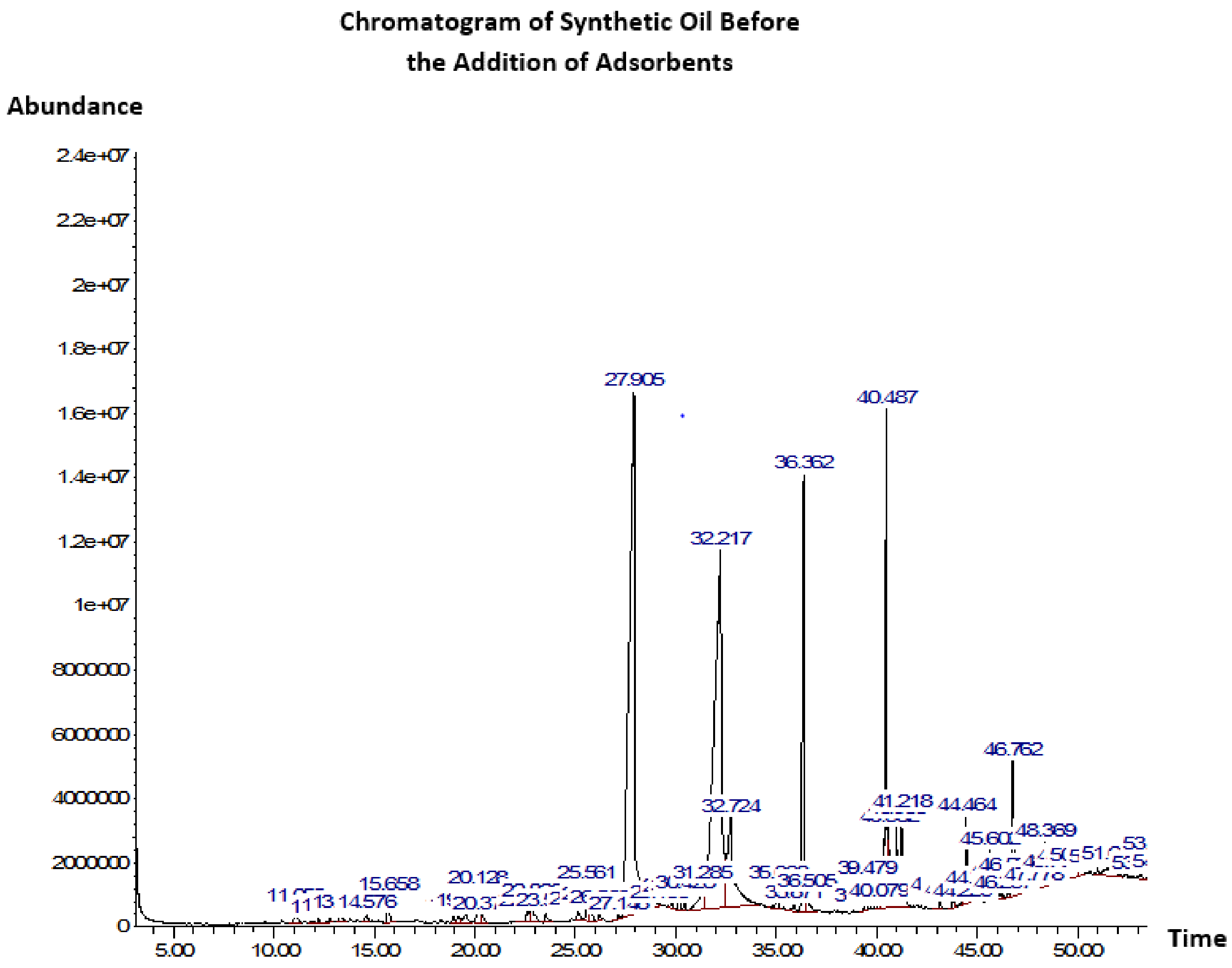
Results and Discussions

- **Before proceeding with further experimental work, the retention time of BaP has to be initially identified.**
- **Using a sample of pure BaP diluted with the solvent (pyridine) at a concentration of 2g/L, the retention time for the organic compound was identified to be approximately 46.88 minutes**



Results and Discussions

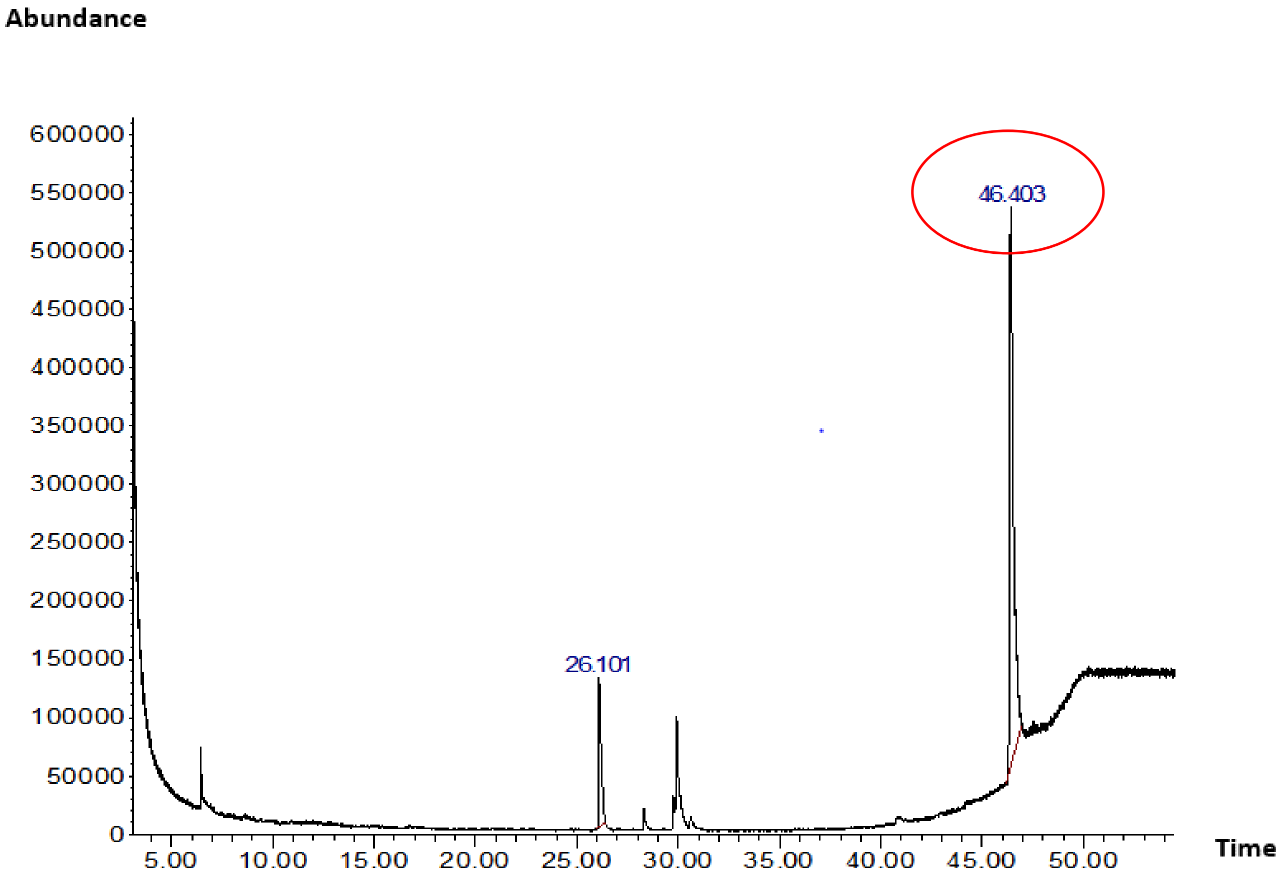
- After determining the retention time of the target pollutant, the preparation of the synthetic stock oil is conducted.
- The synthetic oil is a mixture of BaP and refined palm oil at a concentration of 2g/L.
- As shown at the retention time of 46 minutes, the abundance of BaP detected is approximately 5141317 with an peak absolute area of 351695026



Results and Discussions

- The removal efficiency of bentonite clay was experimented initially. As shown, after the addition of the adsorbent, a significant decrease (82%) of BaP was detected compared to the initial concentration of synthetic oil as indicated by the huge decrease in abundance at the said retention time.

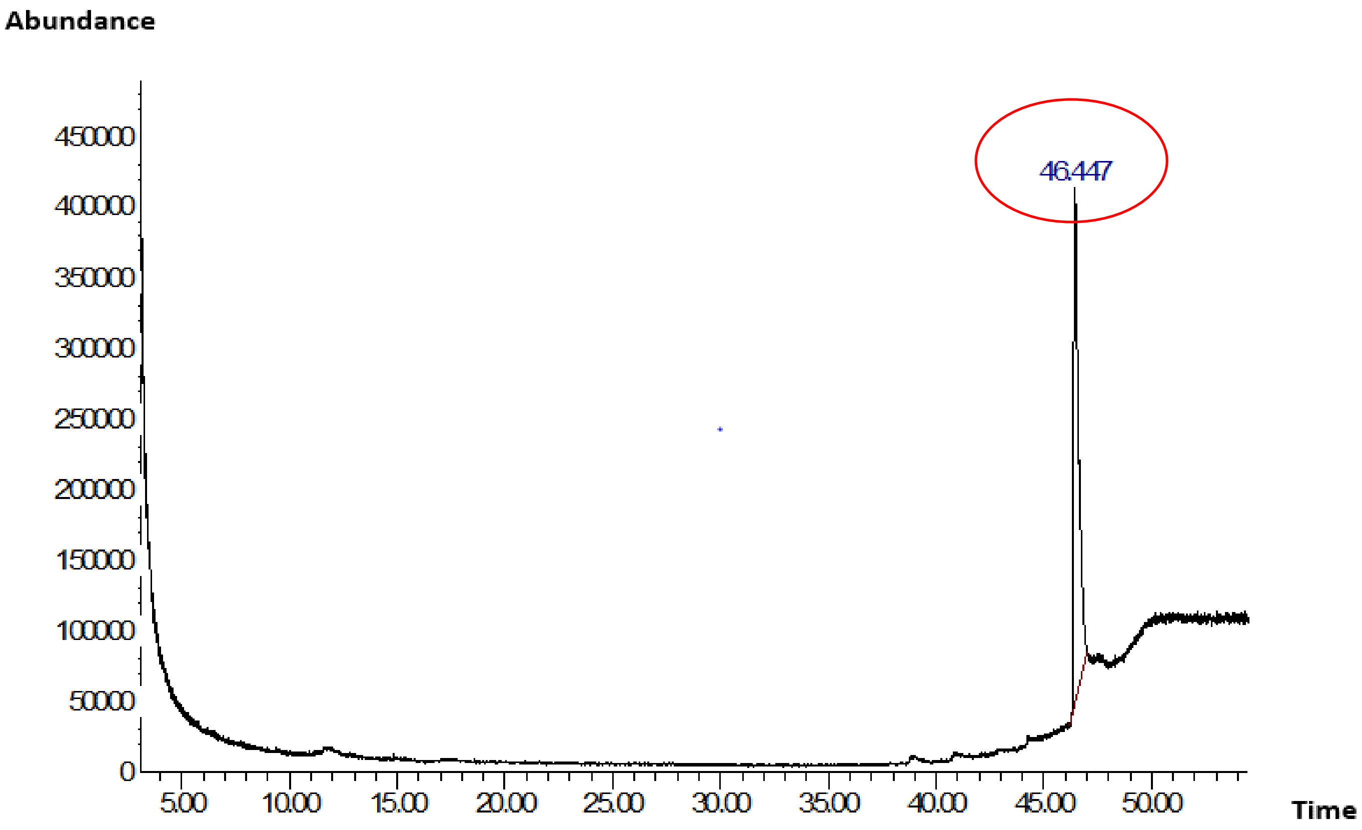
Chromatogram After the Addition of Bentonite



Results and Discussions

- **The removal efficiency of base activated carbon was experimented. As shown, compared to the initial abundance value of 536672 yield by the initial synthetic oil solution, a decrement of 83% of abundance value was detected after the addition of the NaOH activated carbon**

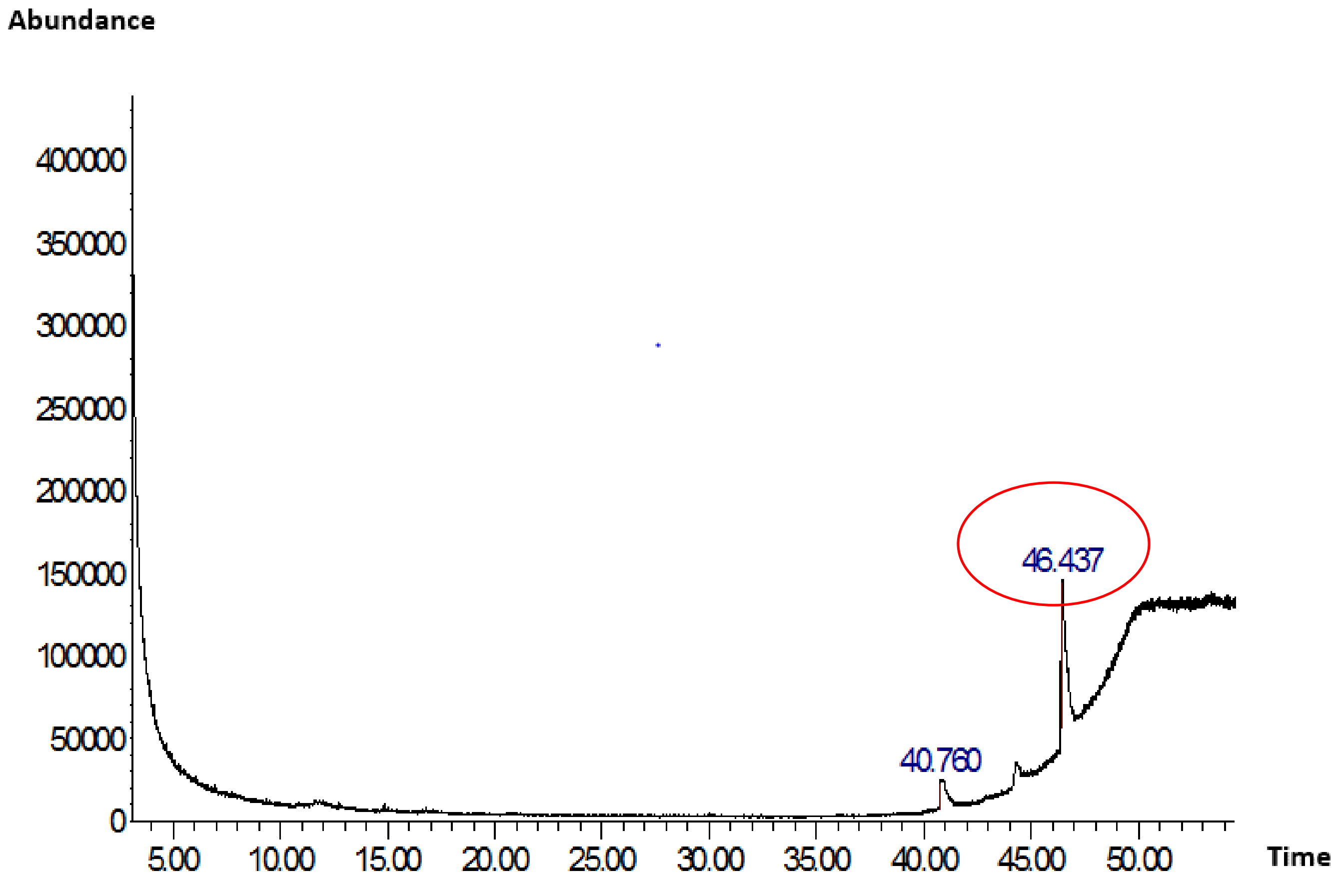
Chromatogram After the Addition of Base Activated Carbon



Results and Discussions

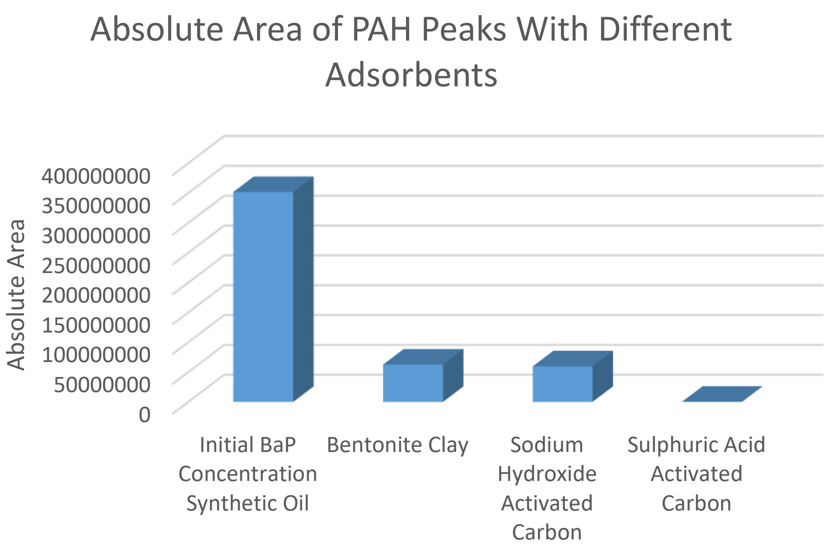
- The removal efficiency of acid activated carbon is shown to provide the most significant removal of PAHs as shown by the chromatogram.
- A PAH removal efficiency of 99% from the initial synthetic oil solution was detected after the addition of acid activated carbon.

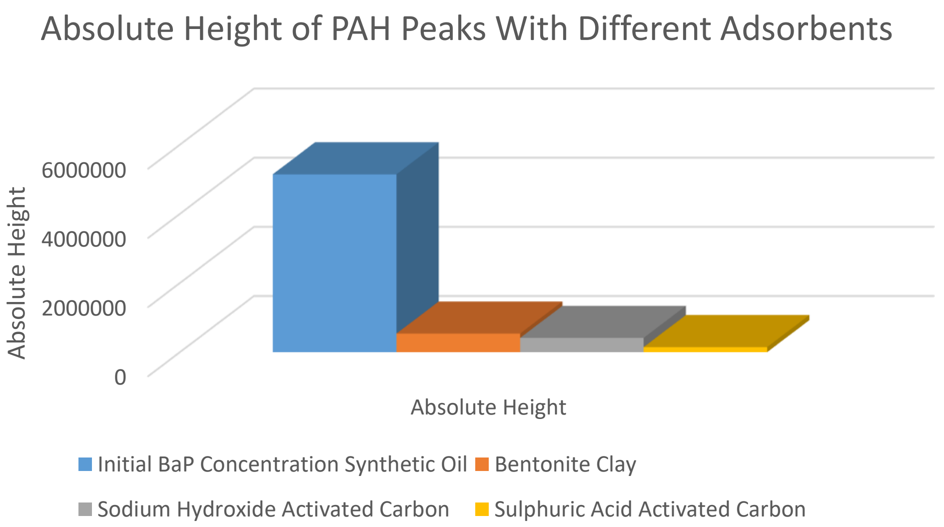
Chromatogram After the Addition of Acid Activated Carbon

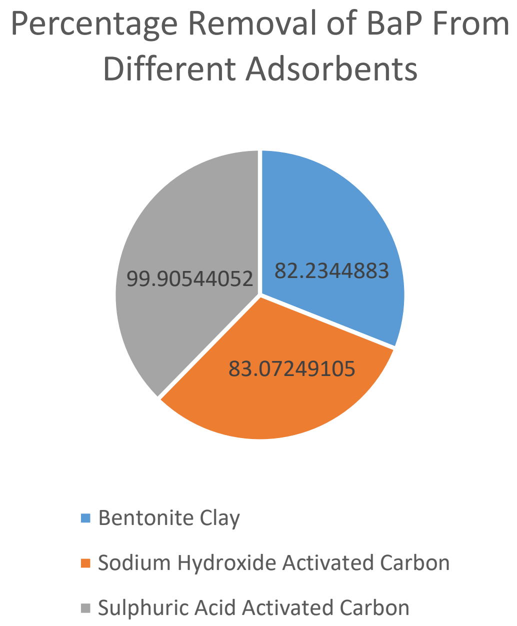


Results and Discussions

	Initial BaP Concentration Synthetic Oil	Bentonite Clay	Sodium Hydroxide Activated Carbon	Sulphuric Acid Activated Carbon
Absolute Area	*351695026*	62480421	59533207	332561
Percentage Removal (%)	-	82.23	83.07	99.91
Absolute Height	*5141317*	536672	411741	146142
Percentage Difference (%)	-	89.56	92.00	97.16







Conclusions

- Bamboo activated carbon has shown to have better adsorption capabilities compared to commercial bleaching earths.
- Acid activated carbon possesses the highest removal efficiency of PAHs, up to 99% removal of BaP. Whereas, base activated carbon and bentonite clay have removal efficiencies of 83% and 82% respectively.
- The high efficiency of acid activated bamboo activated carbon could potentially be attributed to the hydrogen functional groups introduced to the adsorbent by the sulfuric acid, which results to higher removal efficiencies.

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