



## Acid-Modified Adsorbents from Sustainable Green-based Materials for Crude Oil Removal

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### ABSTRACT

This research was carried out to study the sorption capacity of crude oil using acid-modified green-based adsorbents originated from kenaf core and coconut shell. The adsorbent modification was impregnated in the lauric acid, phosphoric acid, and citric acid solution via the conventional method known as wetness impregnation technique. A comparison study of oil sorption capacity between acid-modified kenaf core and acid-modified coconut shell were conducted to identify a better adsorbent for crude oil adsorption. Variable Pressure Scanning Electron Microscopy (VPSEM) equipped with Energy Dispersive X-Ray Spectroscopy (EDX) were utilized to study the morphological characteristics and element compositions for both the unmodified and acid-modified adsorbents. Besides, Fourier Transform Infrared Spectroscopy (FTIR) was used to address the presence, absence, and/or shrink of certain functional groups for both unmodified and acid-modified adsorbents. Based on these three acids used, lauric acid was the best acid modifier than phosphoric acid and citric acid that performed the highest oil adsorption capacity. The VPSEM images of acid-modified adsorbents determined the presence of new pores and thinner walls across the hollow fibres compared to the unmodified adsorbent. Besides, FTIR results proved the presence of new peaks on the green-based adsorbents that confirmed the successful of acid impregnation procedure. This study have proposed that acid-modified green-based adsorbents has high potential to tackle the issues of crude oil spillage. The higher adsorption performance of kenaf core than coconut shell demonstrates that kenaf core can be a low-cost and competitive adsorbent in various applications and expertises.

#### Keywords:

Crude oil, Sorption Capacity, Acid-Modified Adsorbent, Lauric acid, Citric acid, Phosphoric acid

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## 1. Introduction

Crude oil is a naturally occurring mixture of hundreds of different hydrocarbon compounds trapped in subsurface rock. It is a mixture of hydrocarbons, which range from almost solid to gaseous. These hydrocarbons were created millions of years ago from the dead plant and algae material and settled at the bottom of streams, lakes, seas and oceans, forming a thick layer of organic material. Subsequent sedimentation covered this layer and change it into petroleum that extracted from the subsurface today [6]. Crude oil spillage is one of the major disastrous around the world that effects the aquatic life and caused water pollution. One of the world largest oil spill disastrous, The Deepwater Horizon oil spill released 4 million barrels of crude oil into Gulf of Mexico [4].

Numerous approaches for oil spillage cleaning had been reported in the literature which includes the filtration (ultra and micro), reverse osmosis, gravity separation, activated sludge treatment, various flotation methods (dissolved air, column floatation, gas-aphrons, electro and induced air), membrane bioreactors, biological treatment, chemical coagulation, electron-coagulation, coalescences and adsorption. Among all the approaches, adsorption is believed to be the optimal oil spill clean-up as its relatively low cost, excellent oil-removing ability, and eco-friendliness [10].

Adsorption is defined as the adhesion of a chemical species onto the surface of particles. In adsorption process, the gas or liquid particles known as adsorbates, bind to the solid or liquid surface which called as adsorbent. Adsorbent used for oil spillage clean-up can be classified into three basic categories which are inorganic mineral products, organic synthetic products, and organic vegetable products. Inorganic mineral products including zeolites, silica, graphite, and organic synthetic products such as polypropylene and polyurethane. Wood fibre, cotton fibre, kenaf, ground corncobs, and other carbon-based products are classified under the organic vegetable products or known as natural organic sorbents [2].

Organic vegetable or natural organic sorbent had been investigated for the removal of oil spillage due to its advantages which include environmental friendly, cost effectiveness, and relatively easy disposal. Despite of their advantages, several natural sorbents suffer drawback in term of high water uptake due to low hydrophobicity. Therefore, numerous researches had been done to improve the hydrophobicity of natural sorbents. In fact, this research is conducted to study the performance of crude oil adsorption of kenaf core and coconut shell by improving its surface chemistry using acid modification approach. In this study, the surface chemistry for both acid-modified samples were characterized via different characterization techniques such as morphological and structural techniques prior crude oil adsorption study in batch reaction. The hydrophobicity property of the modified green-based material was the main consideration.

## 2. Materials and Method

### 2.1 Material

Kenaf core was procured from National Kenaf and Tobacco Board (NKTB), Kelantan whilst coconut shell was obtained from UTM-MPRC Institute for Oil and Gas. Kenaf core and coconut shell were selected due to its environmental friendly, easily reachable in Peninsular of Malaysia, and more affordable as compared to other adsorbents. All of these materials shall be prepared in a suitable particle size for the experimental purpose.

## 2.2 Preparation of Adsorbents

Kenaf core and coconut shell were milled, grinded, and sieved to obtain smaller particle sizes. The particle sizes were varied in the series of ranges below than 150  $\mu\text{m}$ , 150 to 212  $\mu\text{m}$ , 213 to 600  $\mu\text{m}$ , 601  $\mu\text{m}$  to 1.18 mm, and above 1.18 mm. The sieving procedure was conducted at Shizen Conversion and Separation Technology Laboratory, UTM Kuala Lumpur. The previous study reported by Zaveri [13] found that the particle sizes range of 106 to 840  $\mu\text{m}$  achieves the highest water adsorption rate than other particle sizes. Besides, Zaini [14] also revealed that kenaf core in range of 300 to 500  $\mu\text{m}$  was the best size to adsorb  $\text{CO}_2$  than other particle sizes. Based on these references, this study was proceeded by selecting kenaf core in range of 213 to 600  $\mu\text{m}$ . The sieved samples were kept in a tight container at room temperature in order to prevent any contamination. For the preparation of acid-modified samples, 2 g of kenaf core and coconut shell, respectively was immersed in a 1.0 M and 200 ml of lauric acid, citric acid, and phosphoric acid for six hours in the separated beakers. The mixture was stirred continuously for six hours throughout the impregnation technique by using a magnetic stirrer. The prepared sample was filtered, collected, and dried at 105°C in an oven to remove moisture.

## 2.3 Characterization of Acid-Modified Sample

The prepared acid-modified sample was characterized via Variable Pressure Scanning Electron Microscope (VPSEM) equipped with Energy Dispersive X-ray Spectroscopy (EDX), and Fourier Transform Infrared Spectroscopy (FTIR). VPSEM provides surface topographical of the prepared surface chemistry sample at magnification of 1000X. Meanwhile, EDX analysis was conducted to determine the element compositions of the samples. In addition to that, FTIR was also conducted to identify the presence, absence, or shrink of certain functional groups on the acid-modified sample.

## 2.4 Batch Oil Adsorption Study

The unmodified and acid-modified coconut shell and kenaf core were used as crude oil adsorbents and the experiment was carried out at room temperature. A water-oil mixture was prepared by adding the tap water with crude oil in a fix proportion. Then, 2 g of the prepared acid-modified sample was poured into the water contaminated solution and left without stirring for 60 minutes to make sure all the crude oil is adsorbed by the sample. After 60 minutes, the sample with adsorbed crude oil was removed using a filter paper. The filtered sorbent was dried in oven at 105°C to remove the extra moisture. The batch adsorption test was repeated by using different proportions of crude oil and water from 10000 to 50000 mg/L. The amounts of crude oil adsorbed and oil sorption capacity at different crude oil-water concentrations is determined by weight differences before and after contacting the oil. The oil sorption capacity equation is

$$S = \frac{m_f - m_i}{m_i} \quad (1)$$

where,  $S$  is the oil sorption capacity (g/g),  $m_f$  is the mass of sorbent after crude oil adsorption, and  $m_i$  is the initial mass of sorbent before crude oil adsorption [11,12].

## 2.5 Determination of Volatile Loss

Loss of volatile compound was determined by measuring 0.5 g of crude oil in petri dish and dried in oven at 105°C for six hours. After six hours, the weight of crude oil was measured. This process was repeated until the weight of crude oil was maintain.

## 3. Results and Discussion

### 3.1 Characterization Study of Acid-Modified Samples

#### 3.1.1 Morphological analysis

In this study, VPSEM analysis was conducted to observe the morphology of the acid-modified samples. Table 1 presents the cross-sectional area of the prepared acid-modified kenaf core and acid-modified coconut shell samples. These morphologies would give information on the surface structure available for trapping the oil adsorbates.

From the observed morphologies, all the acid-modified kenaf core and acid-modified coconut shell samples exhibit the thinner wall across the hollowed fibre compared to its precursor. This is due to the stretching of cellulosic compounds caused by the acid modification. The stretching of cellulosic compounds cause the hydrophilic nature of plant to reduce, alternatively increases the hydrophobicity character. As the wall of the hollowed fibre become thinner, the oil sorption capacity is expected to be improved. Similar finding was found by Idan *et al.*, [7] where the pore size for the natural kenaf core fibre is smaller than the modified kenaf core fibre. The pore size is bigger due to dissolved lignin and hemicellulose in the solution.

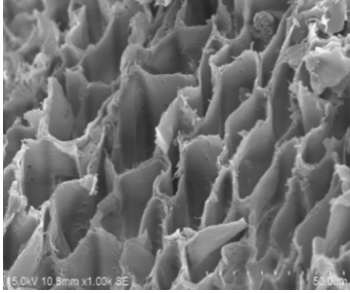
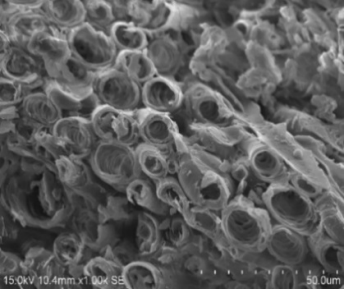
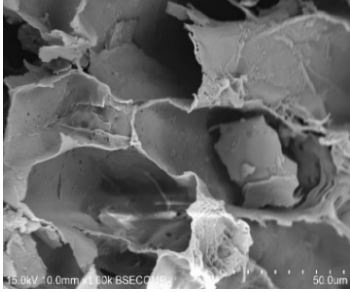
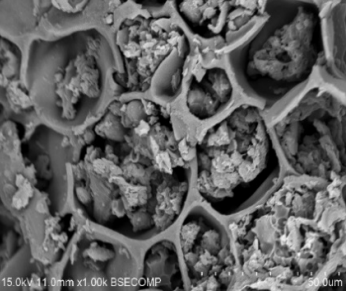
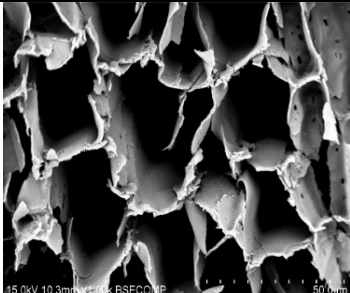

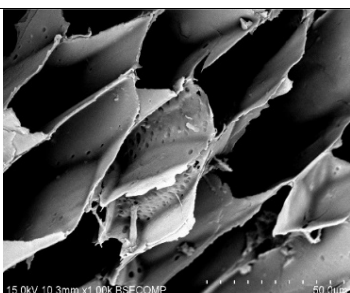

#### 3.1.2 Fourier transform infrared spectroscopy analysis

The FTIR spectra of acid-modified kenaf core samples are shown in Figure 1. In order to distinguish the changes of structure after acid modification procedure, the FTIR spectra of the kenaf core precursor is taking into consideration. The changes of structure could define the effect of acid modification on the surface chemistry of kenaf core.

For all the acid-modified kenaf core, the shrinkages of broad inverted peak in the range of 3300 up until 3500  $\text{cm}^{-1}$  defines the stretching of hydrogen bonding (O-H) of cellulose and hemicellulose compounds after the impregnation of acid modification. The presence of peak at 2912.18  $\text{cm}^{-1}$  and 2855.52  $\text{cm}^{-1}$  for lauric acid-modified, 2923.51  $\text{cm}^{-1}$  for citric acid-modified and phosphoric acid-modified represents the presence of methyl  $\text{CH}_3$  and  $\text{CH}_2$  groups after acid modification [12]. This is caused by the link formation between long alkyl chain of cellulose and hemicellulose compounds. The presence of peaks at 1052.06  $\text{cm}^{-1}$  for the lauric acid-modified, 1052.73  $\text{cm}^{-1}$  for the citric acid-modified, and 1052.37  $\text{cm}^{-1}$  for the phosphoric acid-modified signifies the presence of C–O–C stretching of celluloses and C–O stretching of hemicelluloses [9]. Based on this FTIR spectra analysis, the change of surface chemistry of the acid-modified kenaf core prove that the modification was successfully executed via wetness impregnation technique.

Figure 2 indicates the FTIR spectra of the acid-modified coconut shell samples. The acid-modified coconut shell samples had been compared to the coconut shell precursor to detect any structural changes after completing acid modification procedure.

**Table 1**  
 Cross-Sectional Area of Unmodified and Modified Kenaf Core and Coconut Shell

Sample	Kenaf core	Coconut shell
Precursor (raw)		
Lauric acid-modified		
Citric acid-modified		
Phosphoric acid-modified		

For acid-modified coconut shell samples, an obvious peak was observed at  $3393.33\text{ cm}^{-1}$ ,  $3421.30\text{ cm}^{-1}$ , and  $3399.97\text{ cm}^{-1}$  for lauric acid-modified, citric acid-modified, and phosphoric acid-modified, respectively. These results indicate the same trend as acid-modified kenaf core where the presence of these peaks is due to the stretching of hydrogen bond (O–H) of cellulose and hemicellulose compounds after acid modification procedure. Besides, the presence of a peak observed at  $1693.86\text{ cm}^{-1}$  for lauric acid-modified,  $1643.43\text{ cm}^{-1}$  for citric acid-modified, and  $1638.33\text{ cm}^{-1}$  for phosphoric acid-modified is attributed to the stretching of C=C. The presence of peaks in the range from  $2900\text{ cm}^{-1}$

to  $3000\text{ cm}^{-1}$  for all the acid-modified coconut shell samples is due to the presence of alkyl  $\text{CH}_3$  and  $\text{CH}_2$  groups. Finally, the presence of peaks at  $1000\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$  denotes the presence of C–O–C stretching of celluloses and C–O stretching of hemicelluloses.

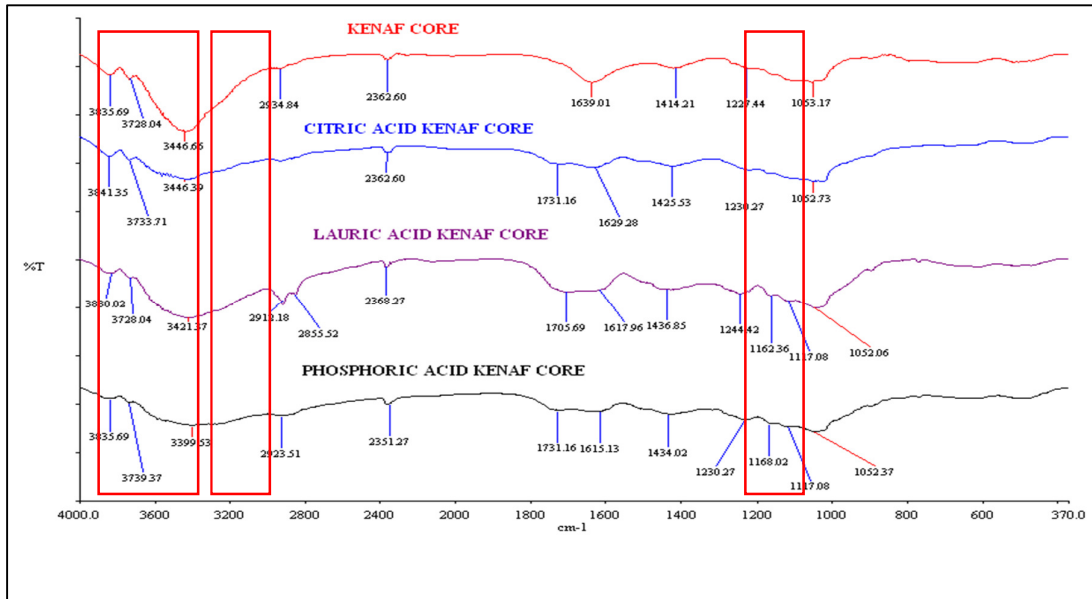


Fig. 1. FTIR results for unmodified and modified kenaf core

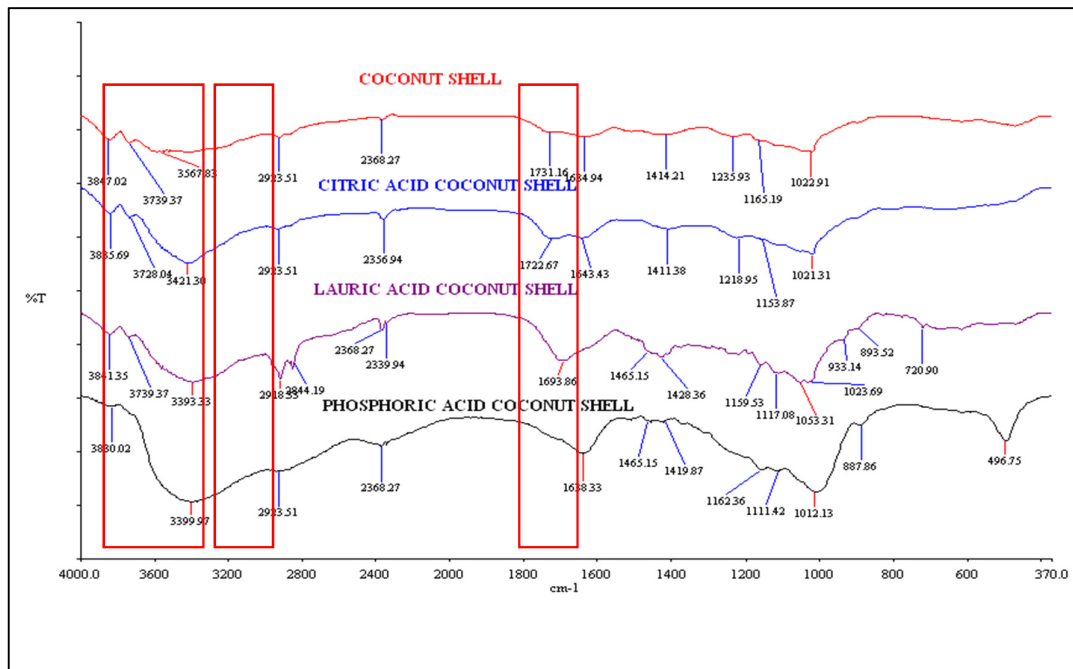


Fig. 2. FTIR results for unmodified and modified coconut shell

### 3.1.3 Energy Dispersive X-Ray Spectroscopy Analysis

The elemental composition analysis provides information on the surfaces chemistry of the prepared acid-modified adsorbent samples. Table 2 (as presented in below) summarizes the elemental compositions present on the surface chemistry of each prepared acid-modified kenaf core and acid-modified coconut shell samples. The element composition of each prepared acid-modified samples were compared to the precursor sample to distinguish the amount of elements that had been increased or degraded after undergone acid-modification procedure.

**Table 2**  
Elemental Composition of Kenaf Core and Coconut Shell

Adsorbents	Elemental Compositions					
	C	O	Na	Mg	K	P
Unmodified Kenaf Core	52.34	46.00	0.43	0.21	1.02	-
Lauric Acid Modified Kenaf Core	63.73	36.03	0.00	0.11	0.13	-
Citric Acid Modified Kenaf Core	54.30	45.70	0.00	0.01	0.00	-
Phosphoric Acid Modified Kenaf Core	55.00	34.16	0.00	0.03	0.00	1.64
Unmodified Coconut Shell	52.34	46.00	0.43	0.21	1.02	-
Lauric Acid Modified Coconut Shell	65.07	34.37	0.00	0.33	0.20	-
Citric Acid Modified Coconut Shell	58.15	41.83	0.00	0.00	0.02	-
Phosphoric Acid Modified Coconut Shell	57.01	37.07	0.00	0.16	0.16	5.60

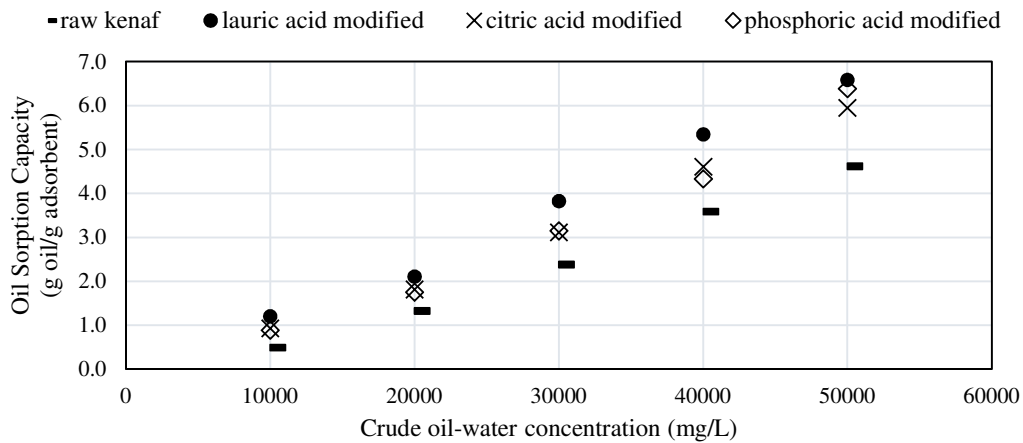
Based on Table 2, it can be seen that the carbon element (C) in the acid-modified kenaf core and acid-modified coconut shell samples is increased and oxygen element (O) is degraded. This is due to the presence of alkyl  $\text{CH}_2$  and  $\text{CH}_3$  functional groups in the lauric acid and citric acid. Both the lauric acid modification samples reveal the highest increment of carbon element (C) among all the modified samples that can be explicated by the presence of long hydrocarbon chain in the lauric acid. For phosphoric acid-modified sample, the presence of phosphate group (P) proved that the kenaf core and coconut shell samples were successfully impregnated using phosphoric acid. According to Bello *et al.* [3], adsorbent with the highest amounts of carbon was the most efficient in adsorbing dyes, heavy metals, and organic pollutants. This EDX data showed that the surface chemistry of acid-modified sample was affected after the impregnation of acid modifier.

### 3.2 Effect of Initial Crude Oil Concentration

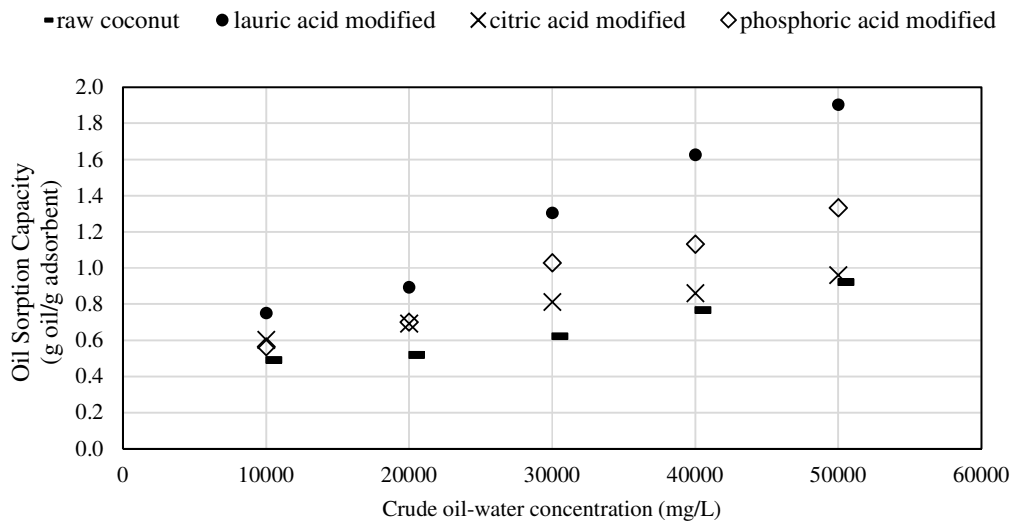
In order to study the adsorption performance of acid-modified natural-based adsorbent, the oil-water concentration was prepared from 10 g/L to 50 g/L. The acid-modified adsorbent was poured without further stirring to let the process running naturally. The crude oil adsorption capacity achieved by acid-modified kenaf core and coconut shell are shown in Figure 3 and 4.

The oil adsorption capacity is the amount of crude oil adsorbed (in gram) per weight of sorbent used (in gram). The oil adsorption capacity is defined as the oil uptake capacity or the sorbency ratio that represents the mass of liquid uptaken per mass of sorbent used [15]. It means that the higher the amount of oil adsorption capacity, the higher the amount of oil that has being adsorbent from the prepared solution. Based on the Figure 3 and 4, the oil sorption capacity of the unmodified and acid-modified kenaf core and coconut shell adsorbents are increased with respect to the increasing of oil-water concentrations. The achieved results also reveal that the acid-modified adsorbents show a better oil sorption capacity than the unmodified adsorbents, valid for both kenaf core and coconut shell adsorbents. The unmodified kenaf core and coconut shell were found to show poor efficiency

for crude oil adsorption with the capacities uptake at 10000 mg/L of 0.88 g/g and 0.57 g/g, respectively.



**Fig. 3.** Crude oil adsorption capacity of unmodified and acid modified-kenaf core adsorbents

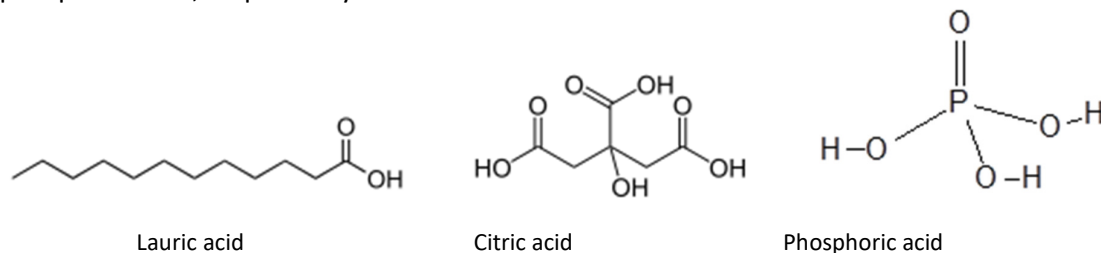


**Fig. 4.** Crude oil adsorption capacity of unmodified and acid modified-coconut shell adsorbents

Generally, the agricultural waste products usually exhibits low sorption capacity due to the presence of numerous hydroxyl groups on its surface [11, 5]. The existence of hydroxyl groups on the surface of kenaf core and coconut shell are hypothesized to repel the crude oil molecules during the adsorption process, thus reduced the oil sorption capacity. At oil-water concentration of 10000 mg/L, the lauric acid modifier presents the higher oil sorption capacity for both kenaf core and coconut shell adsorbents as compared the citric acid and phosphoric acid modified sorbent with the oil capacities for lauric acid-modified kenaf core was 1.20 g/g, and acid-modified coconut shell was 0.75 g/g. Based on this pattern, the oil sorption capacities for those two acid-modified adsorbents were kept increasing with respects to the oil-water concentrations from 10000 until 50000 mg/L. It was



due to the higher hydrophobicity characteristics present by the lauric acid. In order to describe the hydrophobicity characteristics, Figure 5 exhibits the molecular structure of lauric acid, citric acid, and phosphoric acid, respectively.



**Fig. 5.** Molecular structure of different acids used for the modification

As indicated on Figure 5, lauric acid has the longest alkyl chains which promoting the strongest hydrophobicity characteristics to the oil-water mixture. The stronger hydrophobicity character of the modified adsorbent, the higher tendency for the modified adsorbent to repel the molecule of water away from its surface. As a consequence, the higher of oil molecules interacted to the surface, hence increased the oil sorption capacity of the modified adsorbent. Sidik *et al.*, [11] also explicated that the introduction of lauric acid chain to the agricultural waste materials will substitutes the existing hydroxyl groups which then led to the creation of non-polar layer of the surfaces. The presence of these non-polar surfaces increased the hydrophobicity degree as well as the contact area to the oil molecules which was believed to provide the superior sites for the oil adsorption uptake, hence improves the oil sorption capacity of the adsorbent.

#### 4. Conclusion

This study concludes that acid-modified green-based adsorbent demonstrate the higher oil sorption capacity by introducing the non-polar layer on its surfaces. The introduction of this non-polar layer on the surface increased the hydrophobicity degrees of the modified adsorbent, thus enhance the oil adsorption capacity of the acid-modified adsorbent. This study proves that the acid modification technique is one of the improvements that can be used to enhance the oil adsorptive capability of kenaf core and coconut shell.

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