

## Oil Palm (*Elaeis guineensis*) Petiole as a Novel Bio-Matrix for Phenol Removal from Aqueous Phase

<sup>1,2</sup>Ibezim-Ezeani Millicent Uzoamaka, <sup>2\*</sup>Obi Chidi and <sup>2</sup>David Uchechukwu Maxwell

<sup>1</sup> Niger Delta Aqua Research Group, Department of Biochemistry and Chemistry Technology, School of Science Laboratory Technology, University of Port Harcourt, Port Harcourt, P. M. B. 5323, Choba, Rivers State, Nigeria.

<sup>2\*</sup>Physical Chemistry Unit, Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Rivers State, Nigeria

\*Corresponding author: [chidi.obi@uniport.edu.ng](mailto:chidi.obi@uniport.edu.ng)

### Abstract

*This study focuses on the removal of phenol from aqueous phase using oil palm petiole (OPP). Batch operation was carried out to observe the effect of various experimental parameters such as contact time, temperature, pH and initial concentration of phenol. The oil palm petiole (OPP) biomass was characterized using phytochemical screening methods, Atomic Absorption Spectrophotometer (AAS), X-ray diffraction (XRD) technique, Fourier transform Infra-red (FTIR) spectroscopy and scanning electron microscopy. The equilibrium data generated with respect to initial concentration was modeled using Langmuir, Freundlich, and Temkin isotherm equations. The kinetics was studied using the pseudo – first and pseudo – second order equations. The thermodynamics was evaluated using the van't Hoff's equation. The phytochemical screening showed that saponin was abundant in OPP. The AAS analysis showed high content of magnesium. The micro-porous nature of the OPP was evident from the SEM images. The maximum removal efficiency of 99.96% was observed at phenol concentration of 80mg/L. The study showed that Temkin isotherm model was the most suitable for the adsorption process having a correlation coefficient ( $R^2$ ) of 0.953. This result was supported by the pseudo – second order kinetics having a correlation coefficient ( $R^2$ ) of 1.00. This is an indication that chemisorption was the most predominant adsorption process. The thermodynamic studies of the adsorption process showed that  $\Delta H^\circ = 83.56\text{kJ/mol}$ ;  $\Delta S^\circ = 396.49\text{ J/mol/K}$  and  $\Delta G^\circ$  values at different temperatures were – 36.6, – 40.6, – 44.6, – 48.5 and – 52.5kJ/mol respectively. This shows that the adsorption process was spontaneous and endothermic; hence oil palm petiole (OPP) biomass stands to be a potential biomatrix for phenol removal from aqueous medium.*

**Keywords:** *Oil palm petiole, phenol, intermolecular hydrogen bonds, biomatrix, pseudo-second order kinetics, thermodynamic of adsorption*

## Introduction

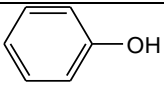
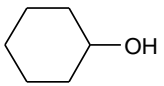
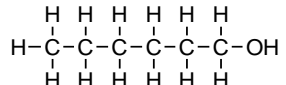
The existence and habitation of different forms of life flourish mainly in conditions of unpolluted atmosphere, green ecosystem, toxically-free terrestrial environment, consumption of uncontaminated foods and water (Ihunwo *et al.*, 2020). These thriving requisites are achievable to a high percentage if:

- (i) Manufacturers give consideration to the use of biocompatible feedstock, starting material(s) and reagent(s) in the design and synthesis of eco-friendly products.
- (ii) Industrialists incorporate feasible production process pathway which will yield relatively little non-toxic waste that is recyclable, reusable and / or biodegradable.
- (iii) Natural and anthropogenic activities are managed in a way that will not be harmful to the components of the earth system.
- (iv) Government authorities, management of institutions and executives of industries and organizations adopt cost efficient and sustainable method of disposal of wastes and effluents in line with local and international regulatory guidelines.

However, the development of fossil fuels and utilization of petrochemical products through human, industrial, domestic, anthropogenic operations; followed by some level of resulting negative consequence(s) on the geosphere, atmosphere, biosphere and hydrosphere are weighing down on the gains of urbanization, industrialization, economic and agricultural prosperity, advancement in science and technology, improved health care and educational facilities, infrastructural development, etc., actualized thus far.

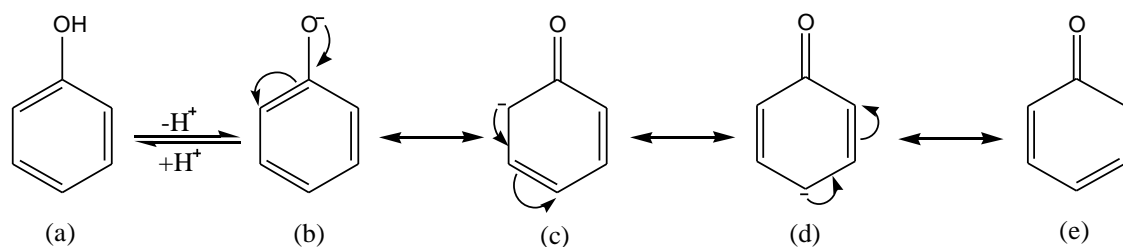
This paper reports the use of oil palm (*Elaeis guineensis*) petiole as a novel bio-matrix for phenol removal from aqueous phase. Phenol (also named as hydroxybenzene) is a volatile transparent-crystalline organic compound having molecular formula, C<sub>6</sub>H<sub>5</sub>OH (Gami *et al.*, 2014) and with its hydroxyl group attachment to the carbon of phenyl group structurally resembling those of cyclohexanol and hexanol to some extent (Table 1).

**Table 1: Bonding of hydroxyl group to carbon in phenol, cyclohexanol and hexanol**

S/ No	Name	Structure	Acid ionization constant	Bonding remark
1	Phenol		$1.12 \times 10^{-10}$	The hydroxyl group is bonded to the sp <sup>2</sup> carbon atom of the phenyl group
2	Cyclohexanol		$1.00 \times 10^{-16}$	The hydroxyl group is bonded to the sp <sup>3</sup> carbon atom of the cyclohexyl group
3	Hexanol		$1.45 \times 10^{-17}$	The hydroxyl group is bonded to the sp <sup>3</sup> carbon atom of the hexyl group

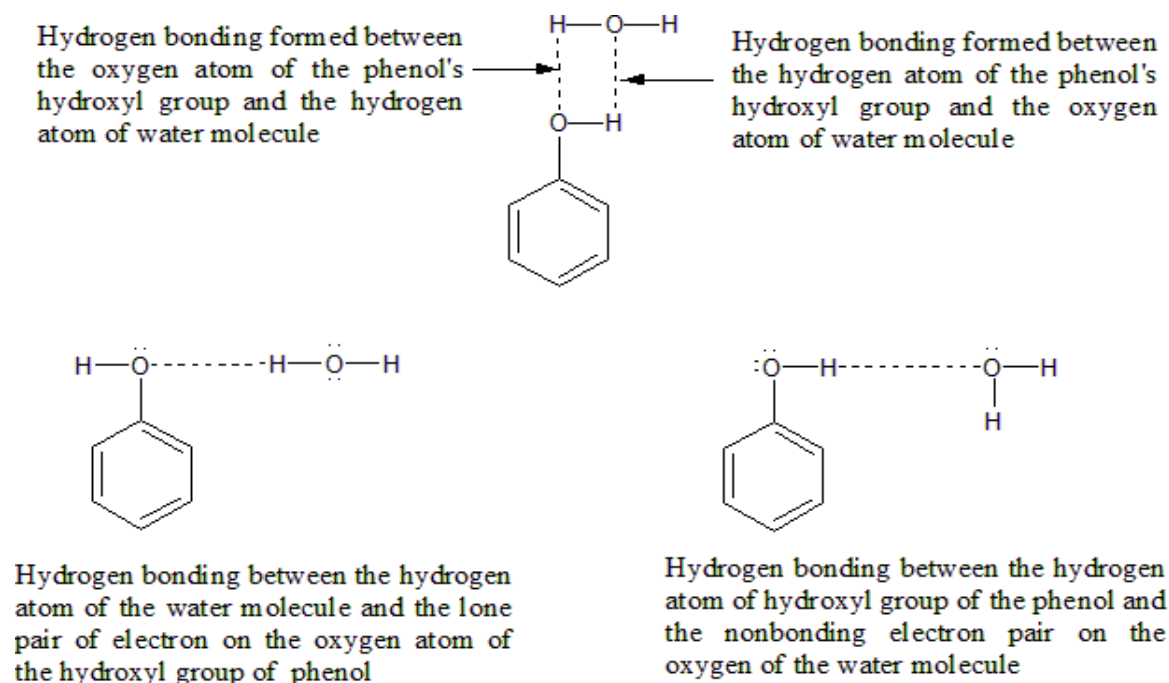
Phenol (Fig. 1a) is weakly acid, but more acidic than its counterparts (cyclohexanol and hexanol); due to the remarkable stability and reactivity acquired by the resonance stabilization of phenoxide

anions (Fig. 1b to 1e) as the negative charge on oxygen delocalizes over the ortho and para carbon positions through the aromatic pi system.



**Fig. 1: Structures of phenol and resonance stabilized phenoxide anions**

However, phenol continues to serve as precursor, intermediate, starting material, reagent and component in varied production processes such as wood and leather preservatives, plastics, antiseptics, explosives, adhesives, dyes, resins, paints, lacquers, oil refining, perfumes, pharmaceuticals, pesticides, xylenols, oils, etc (Gami *et al.*, 2014); and thus, phenol and phenolic particulates constitute fractional amounts in factory effluents from some of these industries, especially those lacking standardized treatment prior to discharge into waterways. The aqueous solubility of phenol in this circumstance is enhanced by the intermolecular hydrogen bonding (Brown *et al.*, 2009) between phenol and water molecule (Fig. 2), as well as the reactivity of phenol moiety at its ortho – and para – positions with molecules in the effluent; and through the course of water flow are distributed into aquatic ecosystem and the terrestrial environment, where the hydrophilic and hydrophobic characteristics of phenol and its derivatives facilitate their persistence, recalcitrance and toxicity in the systems.



**Fig. 2: Hydrogen bonding between phenol and water molecule**

Furthermore, phenolic species exist in staggering quantities within gas flares, fumes of burning refuse dumps, photochemical smog, soot, etc., where they are stabilized by intermolecular hydrogen bonds with non-bonding electron pair on oxygen, nitrogen or fluorine atom in other molecule(s) found in the atmosphere; as well as electrophilic sulphonation, nitration, halogenation, etc. (McMurry, 2012) with sulphur, hydrogen, oxygen, carbon, chlorine, nitrogen and fluorine related radicals, gases, atoms, ions, molecules and compounds which are possible constituents of contaminated air. Thus, through the operations of dynamic forces associated with conduction, convection, gravity, wind, radiation, mechanicochemical activity and diffusion, they become sufficiently dispersed into the atmosphere and then make their way to aquatic and terrestrial biotas, where they exhibit the propensity to translate the contaminant activities of the medium following bioaccumulation (via food chain), gastrointestinal tract absorption (via oral ingestion), respiratory tract absorption (via inhalation) and topical absorption (via dermal contact) into conditions of intense and life-threatening effects on humans (Kulkarni *et al.*, 2013; Meena *et al.*, 2015; Azizi *et al.*, 2017).

Previously reported methodologies for the abatement of phenols include steam distillation, extraction, adsorption, membrane separation, ion exchange, wet-air oxidation, electrochemical oxidation, evaporation, nano – filtration, electro – coagulation, photodecomposition and enzymatic degradation (El – Ashtoukhy *et al.*, 2013; Kulkarni and Kaware, 2013; Bousba and Meniai, 2014; Lakshimi *et al.*, 2016; Moosa *et al.*, 2016; Mohammad *et al.*, 2017). Nevertheless, the implementation of adsorption procedure with locally sourced agro-waste adsorbent material seems more advantageous over other removal techniques due to its relatively easy design, operation and management, process transferability, scale-up and sustainability, adsorbent availability, regeneration and reutilization; coupled with economic viability, high efficiency, sludge minimization, biocompatible and low energy requiring remediation method (Anisuzzaman *et al.*, 2015; Najafpoor *et al.*, 2016; Sarkar and Fakhruddin, 2017; Rahdar *et al.*, 2017; Onyeogulu and Ibezim-Ezeani, 2019; Pat-Okunbor *et al.*, 2019).

Hence, the need for the application of agro-waste material from indigenous plant (such as palm tree) with the potential for conversion to value added products through chemical modification, biotechnology and engineering approach for the removal of noxious substances from aqueous medium. Oil palm petiole (OPP) is one of the biomass (alongside with oil palm empty fruit bunches, oil palm mesocarp fibre, palm kernel cake, shells, oil palm frond and palm oil mill effluent) generated from the processing of palm fruits into oil (Chew and Bhatia, 2008; Baharuddin *et al.*, 2011). Literature has shown that the OPP contains high ligninocellulose fiber which was used commercially in the bioconversion of chemically untreated frond petioles into lignin peroxidase and xylanase-rich enzyme cocktail under solid-state fermentation (Mardawati *et al.*, 2017; Mohamed *et al.*, 2018). The internal structure of OPP has also been evaluated (Windsor-Collins *et al.*, 2008) but there was marginal information on the use of OPP biomass in remediation studies. Palm oil is a mega commodity from palm tree produce in the agricultural sector of Nigeria's economy, especially in the South – South and South – East regions, where they are produced in large volumes for domestic and commercial purposes; while the huge accrued wastes occupy significant portion of space and require reduction and management through transformation into economically laudable products such as sorbent material for remediation process.

This investigation therefore, focuses on identifying the phytochemical composition, morphology and functionality of the OPP, as well as the kinetic, thermodynamic and other influential parameters of adsorption for possible leverage in maximizing its potential as adsorbent in the retrieval of phenol from aqueous phase. Thus, the resolved adsorptive capacity, mechanism and energy requirement from this research finding will serve as bench mark for the utilization of OPP adsorbent in the remediation of phenol contaminated aqueous phase.

## Materials and Methods

### Sample collection and Preparation

Oil palm petiole (Fig. 3) used in this study was obtained from the Unipark campus of the University of Port Harcourt, Rivers State, Nigeria. The oil palm petiole was identified by the Department of Plant Science and Biotechnology Herbarium of the University of Port Harcourt. It was cut from the palm frond of an oil palm tree (*Elaeis guineensis*) and the external layer removed completely. The petiole was divided into sections and dried to constant weight at 105°C for 48 hours. After drying, the sections were ground to obtain a brown powder using a mechanical grinder and passed through a 100 µm sieve. The powdered form was labeled OPP and kept in a desiccator for further use.



**Fig. 3: Oil palm petiole**

### Adsorbate Preparation

Analytical grade reagents were used and the stock standard solution of 1000 mg/L phenol was prepared by dissolving 1.00 g of phenol in 1000 mL of distilled water in a 1000 mL standard flask. Different concentrations of phenol were prepared from the stock standard solution using the dilution formula:

$$C_1V_1 = C_2V_2 \quad (1)$$

Where  $C_1$  = known stock concentration; (1000 mg/L),  $V_1$  = unknown volume of the stock concentration,  $C_2$  = known concentration of the phenol that is to be prepared (i.e. 10 mg/L to 80 mg/L) and  $V_2$  = known volume).

## **Phytochemical Analysis of OPP**

### **Tannins**

The dried powdered sample (0.5 g) of OPP was boiled in 20 mL of water in a test tube and then filtered. A few drops of 0.1% ferric chloride was added and observed for brownish green, to a blue-black coloration. Presence of brownish green or blue-black coloration confirmed the presence of tannins.

### **Flavonoids**

Dilute ammonia (5 mL of 10%) solution was added to a portion of the aqueous solution of the sample, followed by addition of 10 mL conc. H<sub>2</sub>SO<sub>4</sub>. A yellow coloration observed in the solution indicated the presence of flavonoids.

### **Saponins**

The powdered sample (2 g) was boiled in 20 mL of distilled water in a water bath and filtered and 10 mL of the filtrate was mixed with 5 mL distilled water and shaken vigorously for stable persistent froth. The frothing was mixed with 3 drops of olive oil, shaken vigorously for uniformity and was then observed for the formation of emulsion.

### **Glycosides**

The sample solution (5 mL) was treated with 2 mL of glacial acetic acid containing 1 drop of ferric chloride solution (0.1%). This was mixed with 1 mL of conc. H<sub>2</sub>SO<sub>4</sub>. A browning of the interface suggests a deoxysugar characteristic of cardenolodes. A violet ring may appear while in the acetic layer, a greenish ring may form gradually.

### **Steroids**

Acetic anhydride (2 mL) was added to 0.5 g ethanol extract of each of the sample with 2 mL H<sub>2</sub>SO<sub>4</sub>. The color changed from violet to blue or green indicating the presence of steroids.

### **Carbohydrate (Benedict's test)**

The sample solution (8 drops) was added in a test tube containing 5 mL of Benedict's reagent. The mixture was boiled in a water bath for two minutes, and allowed to cool down. The color formed depends upon the amount of reducing sugar present in the mixture; and no color change indicates that carbohydrate was absent.

## **Metal Analysis**

The OPP sample was subjected to digestion using a mixture of 3:1 HCl and HNO<sub>3</sub> prior to metal analysis (Zn, Fe, Ca, Mg, K) using Atomic Absorption Spectrophotometer (Buck Scientific, model 210VGP).

## **Fourier Transform Infrared (FTIR) Spectrophotometric Analysis**

A 2 mg of sample and 200 mg KBr was dried and ground. The mixture was squeezed to form transparent pellets of less than 2 μm. The analysis was carried out using (ATR-FTIR model) spectrophotometer. The background spectrum was collected to form an interferogram and was subsequently converted to frequency data by inverse Fourier transform. Data analysis was done by assigning the observed absorption frequency bands in the sample spectrum to the appropriate normal modes of vibrations in the molecules.

## **Analysis of OPP using X-ray Diffractometer**

X-ray powder diffraction (XRD) was performed to analyze the crystallographic structure of the ground pellets at 298 K. Afterward, 1 g of OPP was packed in an aluminum sample holder and

analyzed with an automated x-ray diffractometer (N8 HORIZON) with a Cu-K $\alpha$  radiation (wavelength =1.789010Å) source operating at voltage of 40 kV (40mA current) in the 2 $\theta$  range from 10 – 55° in steps of 0.05° at a rate of 5° per 10 seconds.

### **Scanning Electron Microscope (SEM) analysis of OPP**

Scanning electron microscope (Verios G4 XHR) was used to resolve the surface morphology of OPP sample before adsorption of thin layer of platinum was sputter-coated on the OPP sample for charge dissipation during SEM imaging. The sputter coater was operated in an argon environment using a current of 6mA for 3 minutes. The coated sample was then transferred to the SEM specimen chamber and observed at an accelerating voltage of 5 kV, eight spot size, four aperture and 15 mm working distance. OPP sample was placed in the path of the electron beam which was continuously deflected into a raster scanning pattern by the deflection coil.

### **Adsorption Studies**

#### **Effect of concentration**

OPP (1 g each) was weighed into eight (8) 100 mL conical flasks and 20 mL of the phenol solutions ranging from 10 – 80 mg/L were added to form mixtures. The mixtures were shaken with a mechanical shaker (180 rpm) at a constant time of 60 minutes at 298 K. The mixtures were filtered into another conical flask and the filtrate was analyzed using Ultraviolet-Visible spectrophotometer (UV – 2600/2700).

#### **Effect of contact time**

OPP (1 g) of sample was weighed into a 100 mL conical flask and 20 mL of 10 mg/L phenol solution was added. The mixture was shaken with a mechanical shaker (180 rpm) for 10 minutes. The procedure was repeated for 20, 30, 40, 50, and 60 minutes respectively at a constant initial concentration of 10 mg/L. At the end of each time, the sample was filtered into another conical flask and the filtrate was analyzed using UV Spectrophotometer.

#### **Effect of pH**

The pH of 10 mg/L phenol solution was initially adjusted to the required pH (i.e. 2, 4, 6, 8, 10, and 12) with either 0.1 M HCl or 0.1 M NaOH. 20 mL of each of the adjusted pH value was measured into the sample bottle containing 1 g of OPP. This was agitated with the use of mechanical shaker (180 rpm) at a constant time of 60 minutes and at a temperature of 298 K. At the end of the adsorption for each pH, the sample was filtered and the filtrate was analyzed using UV Spectrophotometer.

#### **Effect of temperature**

OPP (1 g) was weighed into a 100 mL conical flask and 20 mL of 10 mg/L phenol solution was added. The mixture was shaken with a mechanical shaker (180 rpm) at a temperature of 30°C in a water bath at a constant time of 60 minutes. The procedure was repeated for different temperature of 40, 50, 60, and 70°C using a constant concentration of 10 mg/L. At the end of the process for each temperature, the sample was filtered and the filtrate was analyzed using UV Spectrophotometer.

## Results and Discussion

### Phytochemical Analysis

The phytochemical component of OPP is presented in Table 2.

**Table 2: Qualitative result of phytochemical screening on oil palm petiole**

Sample identity	Tannins	Saponin	Flavonoids	Steroid	Glycoside	Carbohydrate
Palm petiole	+	+++	+	+	++	-

The analysis indicated that saponin is abundant in OPP biomass followed by glycoside. Similar results were reported by Raaman *et al.* (2006) and Abdul *et al.* (2006). Tannins, flavonoids and steroids are also present in OPP; while carbohydrate was observed to be absent. The result revealed that oil palm petiole can be used in emulsion preparation.

### Metal Analysis

The metal composition of OPP is presented in Table 3.

**Table 3: Metal compositions of oil palm petiole**

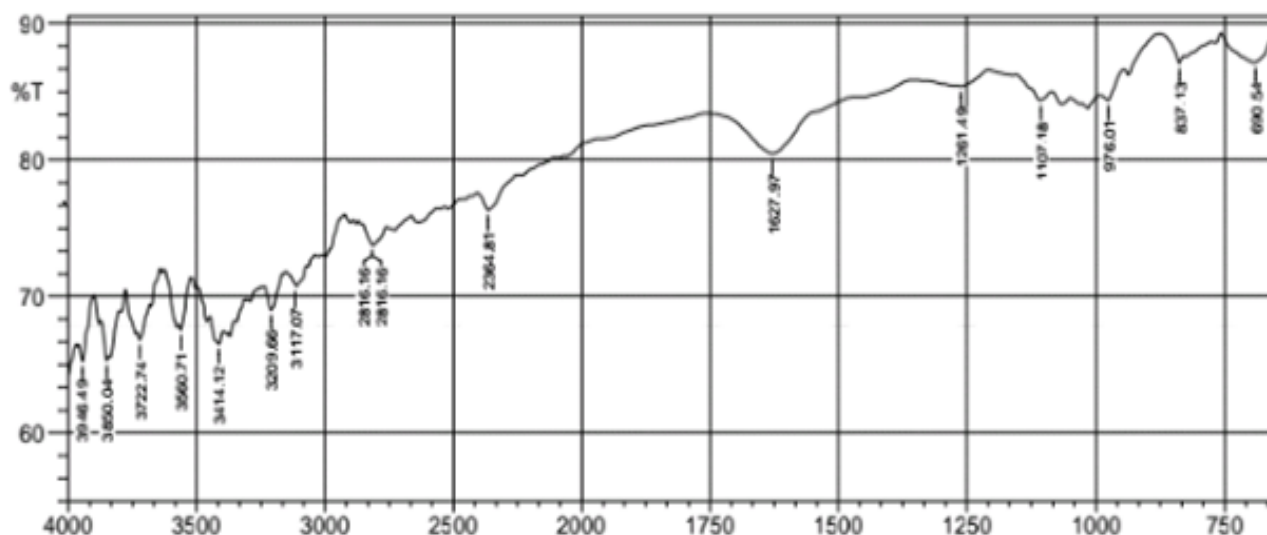
Sample identity	Zn (mg/kg)	Fe (mg/kg)	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)
Palm petiole	10.05	343.25	641.05	697.50	1079.00

The result of metal analysis showed that OPP is very rich in magnesium followed by potassium, calcium and iron. The value for zinc was very low compared to other metals. Generally, the result indicated that OPP biomass can be used both as alternative feed source to supplement the nutrient requirements for poultry (Hassan and Yeong, 1999) and for soil amendment to argument the nutrient needs of plant (Loh *et al.*, 2013).

### FTIR Analysis

The vibrational bands of OPP and its functional groups are presented in Fig. 4 and Table 4 respectively. At the mid infra-red evaluation ( $1400\text{ cm}^{-1} - 400\text{ cm}^{-1}$ ), C-Cl, C-H, C=C, C-O, and  $-\text{CH}_3$  are present. Above the mid infra-red ( $1400\text{ cm}^{-1} - 4000\text{ cm}^{-1}$ ), C=C, O=C=O, C-H, N-H (amide), O-H (acid), N-H (amine) and O-H (alcohol) are present.





**Fig. 4: FTIR spectrum of OPP**

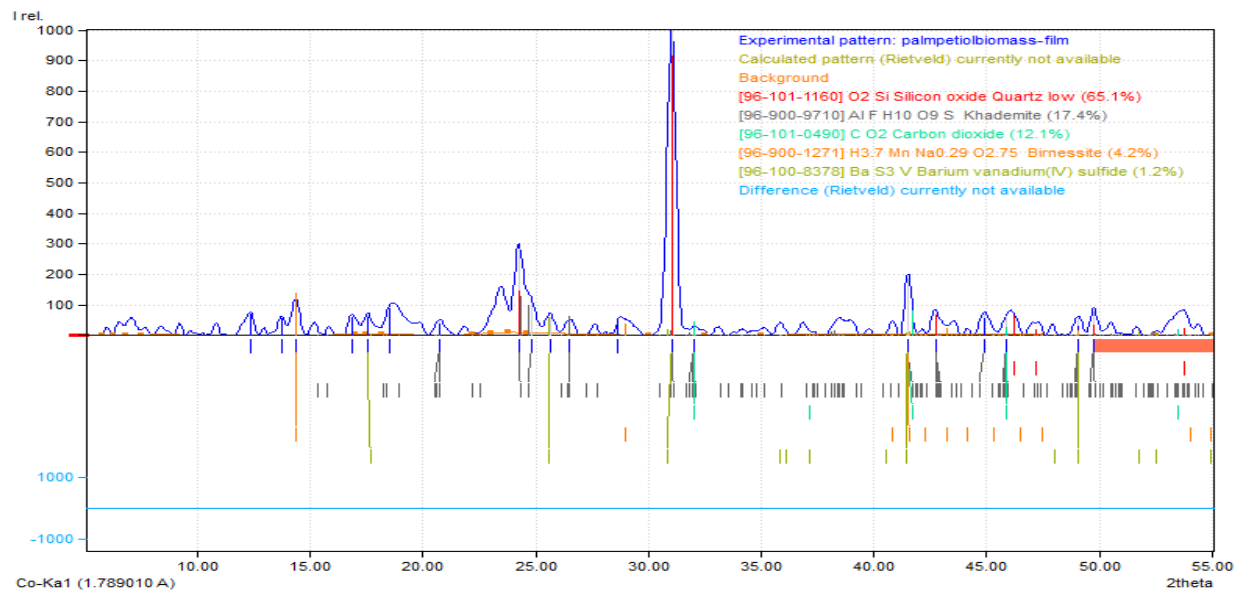
**Table 4: FTIR peaks and predicted functional groups**

S/N	Peak	Predicted functional groups
1	690.54	C-Cl
2	837.13	C-H
3	976.01	C=C
4	1107.18	C-O
5	1261.49	-CH <sub>3</sub>
6	1627.97	C=C
7	2364.81	O=C=O
8	2816.16	C-H
9	3117.07	N-H (amide)
10	3209.66	O-H (acid)
11	3414.12	N-H (amine)
12	3560.71	
13	3722.74	O-H (Alcohol)
14	3850.04	
15	3946.49	

### XRD Analysis

The XRD spectrum in log scale is shown in Fig. 5 and the pattern correspond to SiO<sub>2</sub>, AlFH<sub>10</sub>O<sub>9</sub>S, CO<sub>2</sub>, H<sub>3.7</sub>MnNa<sub>0.29</sub>O<sub>2.75</sub> and BaS<sub>3</sub>V as shown in Table 5.

On the lower part of the plot, the spectra components of the most frequent secondary phases were given (Rosa *et al.*, 2012).



**Fig. 5: XRD spectra of OPP**

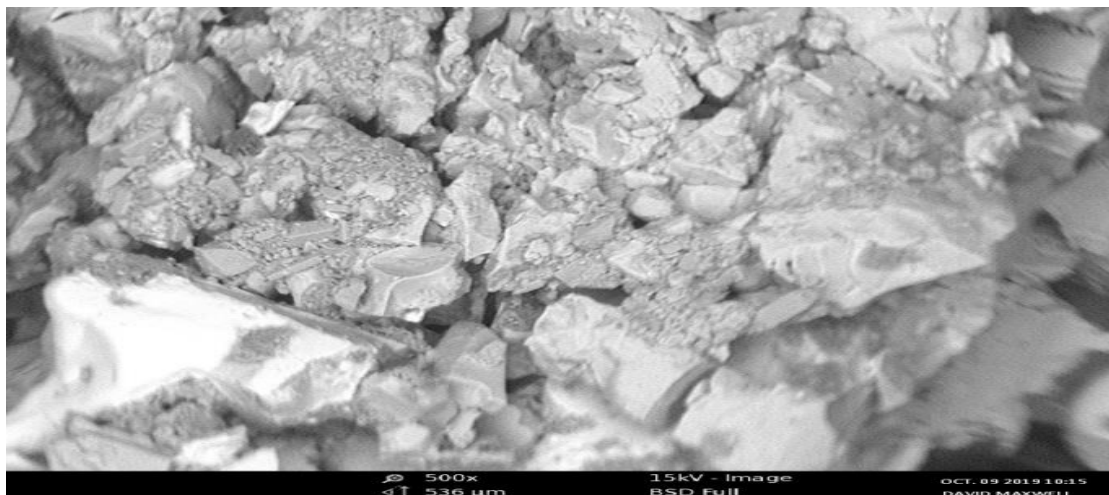
**Table 5: Mineral characterization of OPP by XRD analysis**

Index	Amount (%)	Name	Formula sum
A	65.1	Silicon oxide Quartz low	SiO <sub>2</sub>
B	17.4	Khademite	Al F H <sub>10</sub> O <sub>9</sub> S
C	12.1	Carbon dioxide	CO <sub>2</sub>
D	4.2	Birnessite	H <sub>3.7</sub> Mn Na <sub>0.29</sub> O <sub>2.75</sub>
E	1.2	Barium vanadium (IV)sulfide	Ba S <sub>3</sub> V

Room temperature X-ray diffraction result indicated that the samples were composed of trigonal (hexagonal axes) phase with lattice parameters  $a = 4.9100 \text{ \AA}$ ,  $b = 0$  and  $c = 5.4000 \text{ \AA}$  for silicon oxide; orthorhombic phase with lattice parameters  $a = 11.1810 \text{ \AA}$ ,  $b = 13.0480 \text{ \AA}$  and  $c = 10.8850 \text{ \AA}$  for khademite; cubic phase with lattice parameter  $a = 5.6200 \text{ \AA}$ ,  $b = 0$  and  $c = 0$  for carbon dioxide; monoclinic phase with lattice parameters  $a = 5.1740 \text{ \AA}$ ,  $b = 2.8500 \text{ \AA}$  and  $c = 7.3360 \text{ \AA}$  for birnessite and hexagonal phase with lattice parameters  $a = 6.7192 \text{ \AA}$ ,  $b = 0$  and  $c = 5.6188 \text{ \AA}$  for barium vanadium (IV) sulfide. No peaks of secondary phases were present.

### SEM Analysis

The morphological structure of OPP before phenol adsorption as presented in Fig. 6 showed microporosity. Chen *et al.* (2017) and Joseph *et al.* (2007) in their work on fast and slow adsorption of carbamazepine on biochar reported similar result.

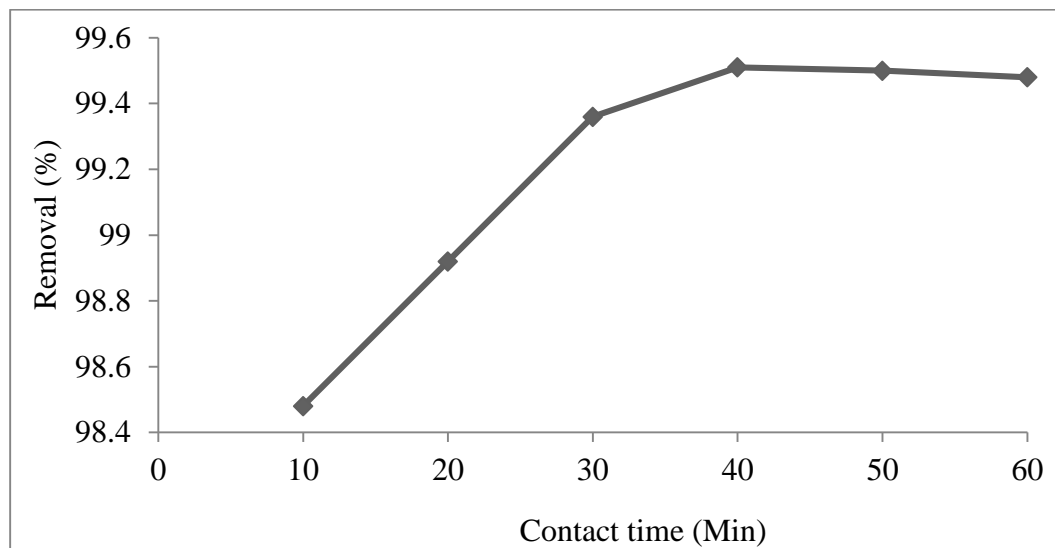


**Fig. 6: Microgram of OPP before adsorption**

### Adsorption Evaluation

#### Contact Time Effect

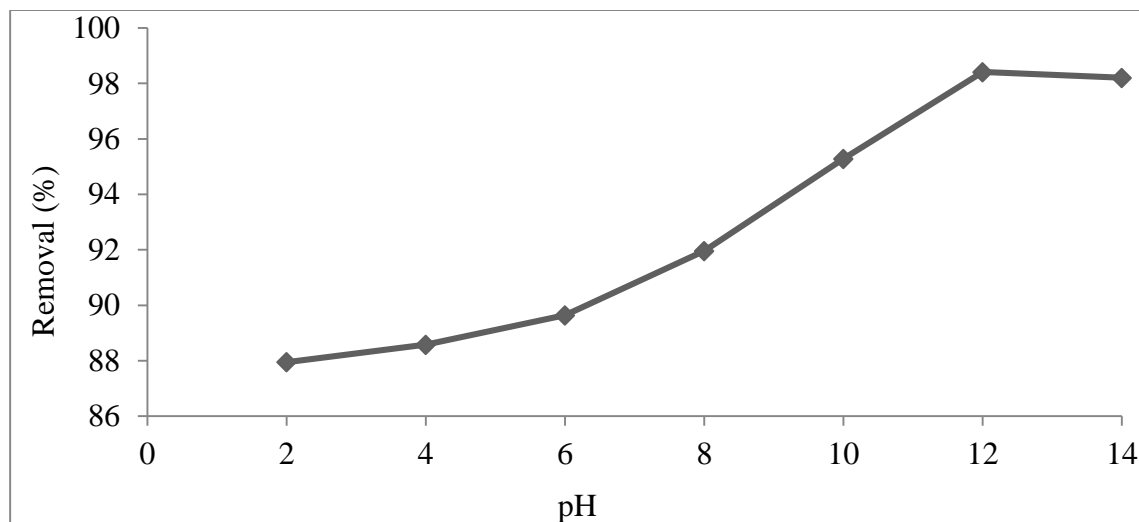
The amount of phenol removed at equilibrium time as shown in Fig. 7 reflected optimum removal efficiency under the working conditions. The result also revealed that the process of removal with respect to time followed three (3) steps which include the fast initial step, slow saturation step and saturation step. This interesting phenomenon was due to the fact that there were large numbers of vacant sites during the threshold of the removal process and after a time frame; the remaining vacant sites were difficult to be occupied due to the competition between the molecules on the surface of the adsorbent and the aqueous phase. Radhika and Palanivelu (2006), Hameed (2007) and Sidik *et al.* (2012) reported similar trend while working with trichlorophenol (TCP) on activated clay, coconut-based activated carbon and modified oil palm leaves respectively. The optimum time for phenol removal was observed at 40 minutes with 99.51% removal efficiency.



**Fig. 7: Effect of contact time on rate of phenol removal by OPP at 298K**

#### **Effect of pH**

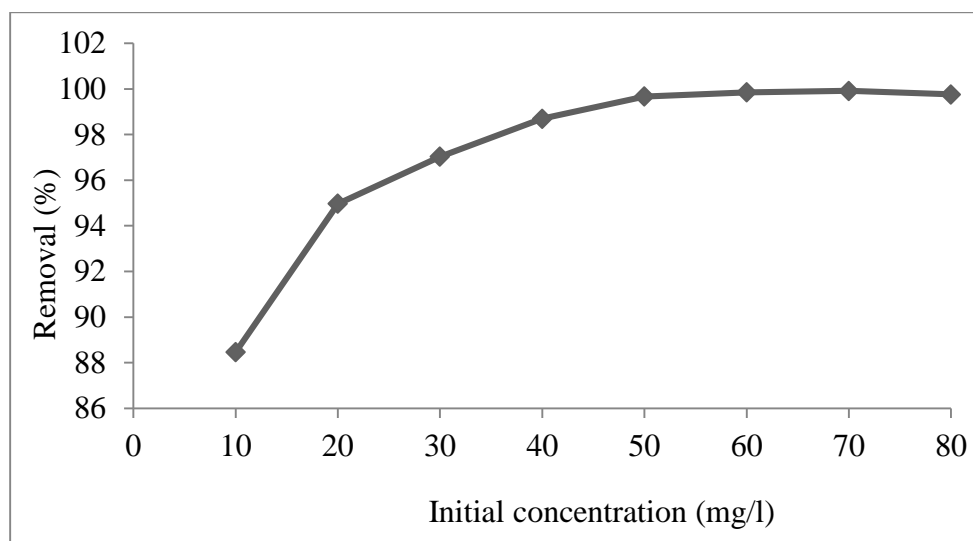
The pH of the solution has a significant impact on the removal of phenol since it influences the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate (Imamoglu and Tekir, 2008). It was noticed in Fig. 8 that the removal efficiency was slow at pH 2 – 6 and rapid from pH 7 – 12, showing that higher pH (basic medium) favored the removal of phenol using OPP. However, the percentage removal of phenol was relatively constant after pH 12; thus, the maximum adsorption was obtained at pH of 12. Sidik *et al.* (2012) reported similar trend on modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal.



**Fig. 8: Effect of pH on rate of phenol removal with OPP at 298K**

### Effect of Initial Phenol Concentration

It was observed that the removal efficiency was rapid at initial phenol concentration of 10 – 40 mg/L as shown in Fig. 9; which became relatively slower from 50 – 80 mg/L concentrations. The result of effect of initial concentration showed that the percentage removal increases with increase in the initial phenol concentration and at 60 – 80 mg/L reached a constant value beyond which no more phenol was further removed from the aqueous phase (Tan *et al.*, 2009). This behavior was evident due to concentration gradient arising from the driving force caused by the mass transfer built by the adsorbate – adsorbent association. The result showed that the maximum removal percentage of phenol was 99.91% at phenol initial concentration of 70 mg/L.

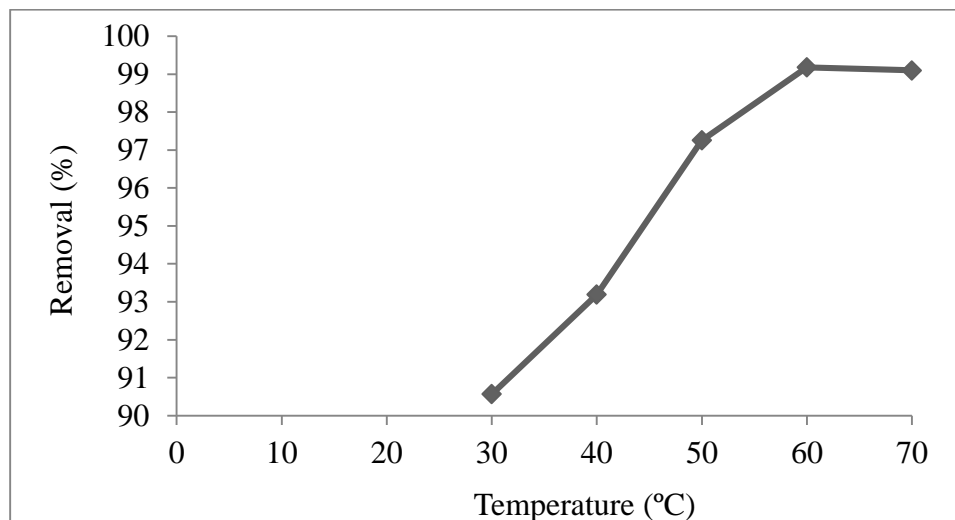


**Fig. 9: Effect of initial concentration on rate of phenol removal with OPP at 298K**

### Effect of temperature

The increase in temperature from 30 – 70°C for all the initial concentrations as shown in Fig. 10 revealed that the adsorption process was endothermic (Karthikeyan *et al.*, 2005; Wang and Zhu, 2007). Reports have shown that increase in temperature caused increase in the diffusion rate of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle. This might be due to the increase in the number of pores on the adsorbent surface. The high temperature was observed to reduce the viscosity of the outer surface of the adsorbent (OPP), due to increase in the kinetic energy of phenol molecules; and as a result phenol molecules were easily adsorbed on the adsorbent surface (Wang and Zhu, 2007; Maleki *et al.*, 2010).

In this study, it was observed that optimum removal efficiency occurred at 60°C.



**Fig. 10: Effect of Temperature on rate of phenol removal with OPP at 298K**

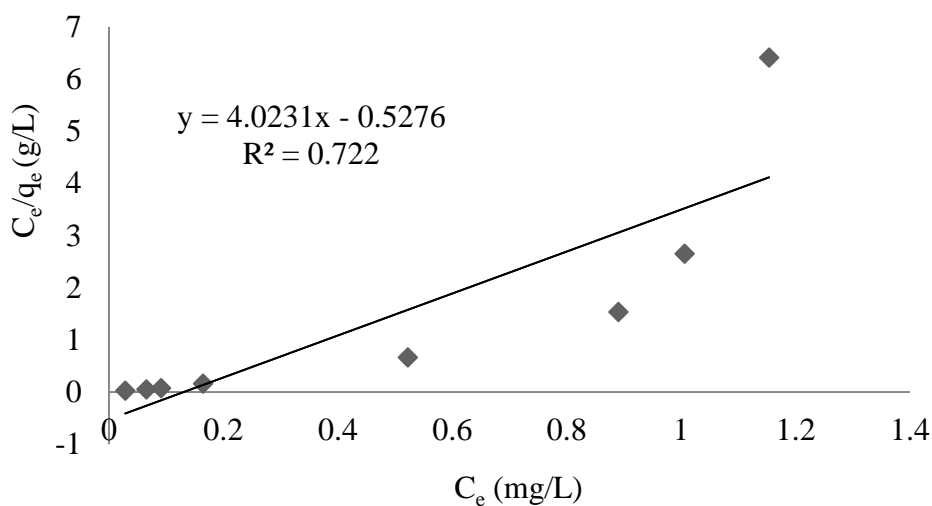
### Adsorption Isotherms of Phenol onto OPP

#### Langmuir Adsorption Isotherm model

The linear mathematical expression of Langmuir shown in equation 1 was used for the study of monolayer behavior.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (1)$$

Where  $C_e$  is the equilibrium liquid-phase concentration,  $q_e$  is the amount of heavy metal ions (mg/g) adsorbed at equilibrium,  $q_m$  (mg/g) is the monolayer adsorption capacity, and  $K_L$  is the Langmuir constant. The  $q_m$  and  $k_L$  values were determined from the intercept and slope of the line obtained by plotting  $C_e/q_e$  against  $C_e$  respectively.



**Fig. 11: Langmuir adsorption isotherm plot for the removal of phenol by OPP**

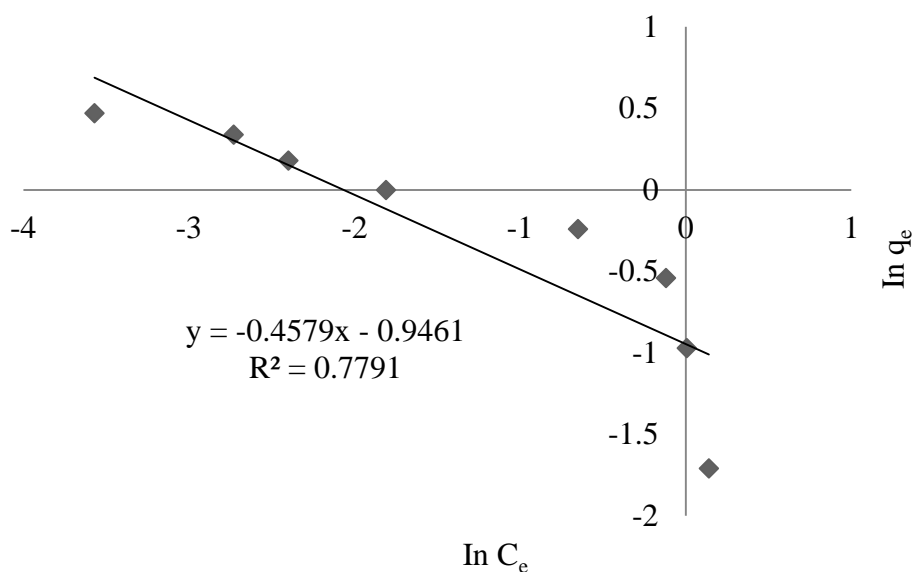
The Langmuir plot presented in Fig. 11 showed a relatively weak linear correlation having correlation coefficient ( $R^2$ ) of 0.722. The monolayer adsorption capacity ( $q_m$ ) was computed as 0.248 mg/g and Langmuir constant ( $k_L$ ) was found to be -7.633 L/mg. The Langmuir isotherm represents the equilibrium distribution of adsorbate between the solid and liquid phases (Dada *et al.*, 2012).

### Freundlich Adsorption Isotherm Model

The linear mathematical expression of Freundlich model used in this study is presented in equation 2 as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

Where  $K_F$  and  $n$  are constants obtained from the slope and intercept of a plot of  $\log q_e$  against  $C_e$ . The Freundlich plot provided in Fig. 12 also showed a relatively weak linear correlation having  $R^2$  of 0.779. The parameter  $n$  applied in predicting whether the adsorption process is favorable or not, was found to be -2.188 and the Freundlich constant ( $k_F$ ) was found to be 0.388 mg/g. This isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface (Hutson and Yang, 2000).



**Fig. 12: Freundlich adsorption isotherm plot for the removal of phenol by OPP**

### Temkin Adsorption Isotherm Model

The Temkin linear equation used in this study is expressed as:

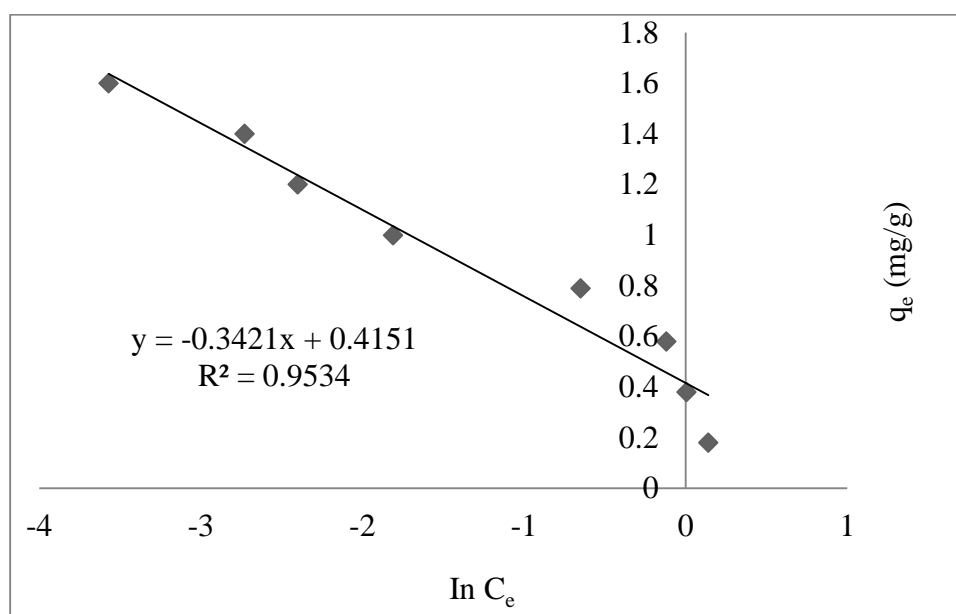
$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (3)$$

Where  $R$  is universal gas constant,  $T$  is absolute temperature,  $A_T$  is Temkin binding equilibrium constant in L/mol; the values obtained from this corresponds to the highest possible binding energies,  $b_T$  is related to the heat of adsorption.

The investigation is carried out by plotting  $q_e$  against  $\ln C_e$  and the  $b_T$  and  $A_T$  values were determined from the slope and intercept of the plot and presented in Table 6.

The result presented in Fig. 13 showed that the heat of adsorption of the interaction between the adsorbate and adsorbent decreased linearly as a result of increase in the surface coverage (Shahbeig *et al.*, 2013; Muhammad *et al.*, 2015).

Temkin adsorption isotherm model is based on the following assumptions:(i) the heat of adsorption of the surface molecules decreases linearly rather than logarithmically with coverage (ii) the adsorption process is characterized by a uniform distribution of binding energies at the adsorbent surface and (iii) this model covers the adsorbate – adsorbent interaction (Muhammad *et al.*, 2015). The Temkin constant related to heat of sorption (b) was computed as  $-0.342$  and this buttressed the fact the removal of phenol using OPP was endothermic since  $B = -\Delta H$ . The Temkin isotherm constant ( $b_T$ ) was determined to be  $-7.25 \times 10^3 \text{ kJmol}^{-1}$ , and Temkin isotherm equilibrium binding constant ( $A_T$ ) was calculated to be  $0.297 \text{ Lmg}^{-1}$ .



**Fig. 13: Temkin adsorption isotherm plot for the removal of phenol by OPP**



**Table 6: Constants for adsorption isotherm models**

Model	Values
<b>Langmuir</b>	
$q_m(\text{mg/g})$	0.248
$k_L(\text{L/mg})$	- 7.633
$R^2$	0.722
<b>Freundlich</b>	
$k_F(\text{mg/g})$	0.388
$n$	- 2.188
$R^2$	0.779
<b>Temkin</b>	
$b$	- 0.342
$b_T(\text{kJ/mol})$	$7.25 \times 10^3$
$A_T(\text{L/mg})$	0.297
$R^2$	0.953

### Kinetics studies

The kinetics of adsorption data was investigated to understand the dynamics of the adsorption process in terms of the order.

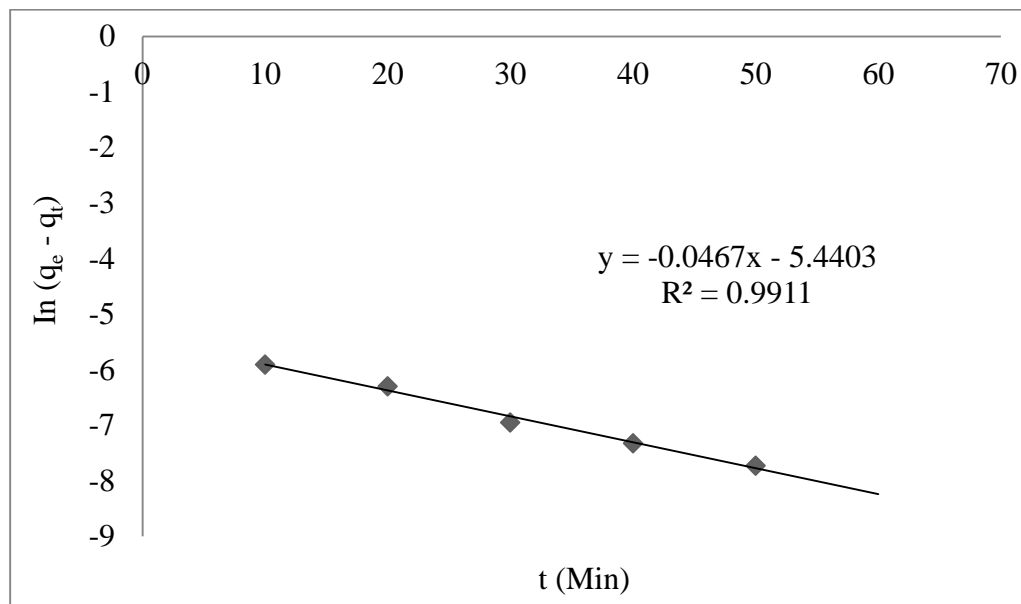
### Pseudo-first order kinetic model

The linear expression of the pseudo first – order kinetic model proposed by Lagergren (Qu *et al.*, 2009; Kumar and Min, 2011) for adsorption is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

Where  $q_t$  is adsorption capacity at time,  $t$  (mg/g) and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant.  $q_e$  and  $k_1$  were determined from the intercept and slope of the plot of  $\log (q_e - q_t)$  versus time.

The pseudo – first order plot as shown in Fig. 14 showed linear correlation with correlation coefficient ( $R^2$ ) = 0.991; and the experimentally deduced equilibrium adsorption capacity ( $q_{e(\text{expt.})}$ ) for the pseudo first – order process was  $4.34 \times 10^{-3}$  mg/g, which did not conform with the calculated equilibrium adsorption capacity ( $q_{e(\text{calc.})}$ ) which was found to be 0.19968 mg/g.



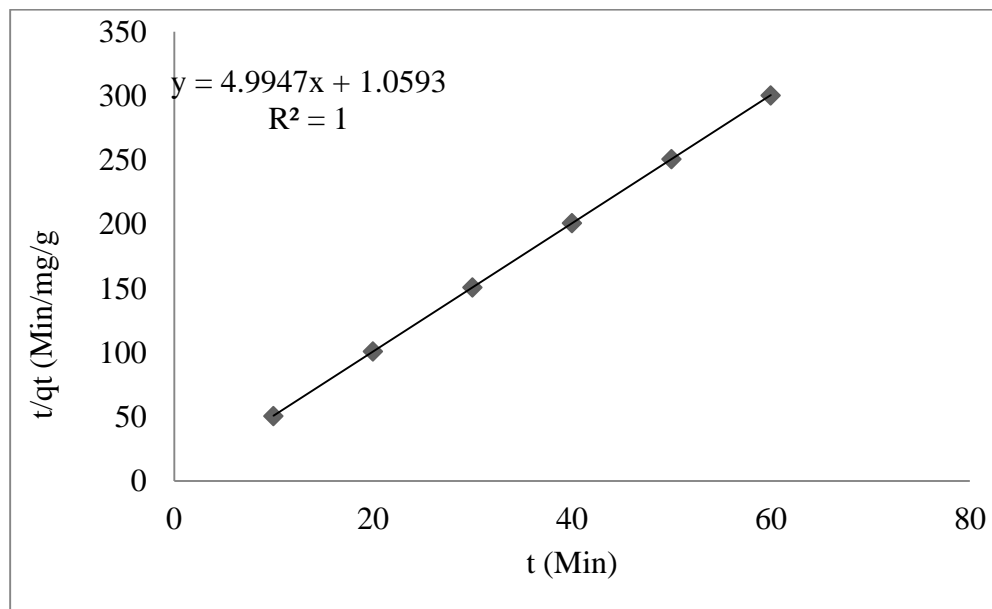
**Fig. 14: Pseudo-first order plot for phenol adsorption**

#### Pseudo-second order kinetic model

The pseudo second – order kinetic model equation was applied in this study (Ho and McKay, 1999; Tang *et al.*, 2012; Liu *et al.*, 2018) and its linear form is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where  $k_2$  (gmol/min) is the rate constant, the values of  $k_2$  and  $q_e$  were deduced from the slope and intercept of the plots of  $t/q_t$  versus time. The experimental data represented in Fig. 15 was better described by pseudo – second order model with  $R^2 = 1.00$  than pseudo – first order model. This suggests that chemisorption was the dominant mechanism, and that the result of the equilibrium study followed Temkin adsorption isotherm model. Further perusal of the tabulation (Table 7), revealed that the experimentally deduced equilibrium adsorption capacity ( $q_{e \text{ (expt.)}}$ ) for the pseudo second – order process was found to be 0.200 mg/g and conformed relatively closer to the calculated equilibrium adsorption capacity ( $q_{e \text{ (calc.)}}$ ) which was found to be 0.19968 mg/g when compared with that of pseudo first – order. Nur *et al.* (2012) reported similar trend of behavior on the removal methylene blue dye in aqueous solution using raw empty fruit bunch biomass.



**Fig. 15: Pseudo-second order plot for phenol adsorption**

The kinetic constants, the experimentally deduced equilibrium adsorption capacity ( $q_e$  (expt.)) and correlation coefficients of these models were calculated and presented in Table 7.

**Table 7: Pseudo-first and pseudo-second order kinetic constants**

Pseudo-first order kinetic model			Pseudo-second order kinetic model		
$k_1$ (min <sup>-1</sup> )	$q_e$ (expt.)(mg/g)	$R^2$	$k_2$ (g/mg/min)	$q_e$ (expt.)(mg/g)	$R^2$
0.046	$4.34 \times 10^{-3}$	0.99	23.810	0.200	1.00

### Thermodynamic Studies

Thermodynamic parameters such as the free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes during adsorption were evaluated using equations 6 – 8 (Sujana *et al.*, 2009). Plot of  $\ln k_c$  versus  $1/T$  (Fig. 16) was applied in deducing the value of  $\Delta H^\circ$  from the slope and  $\Delta S^\circ$  from the intercept of plot, and presented in Table 8.

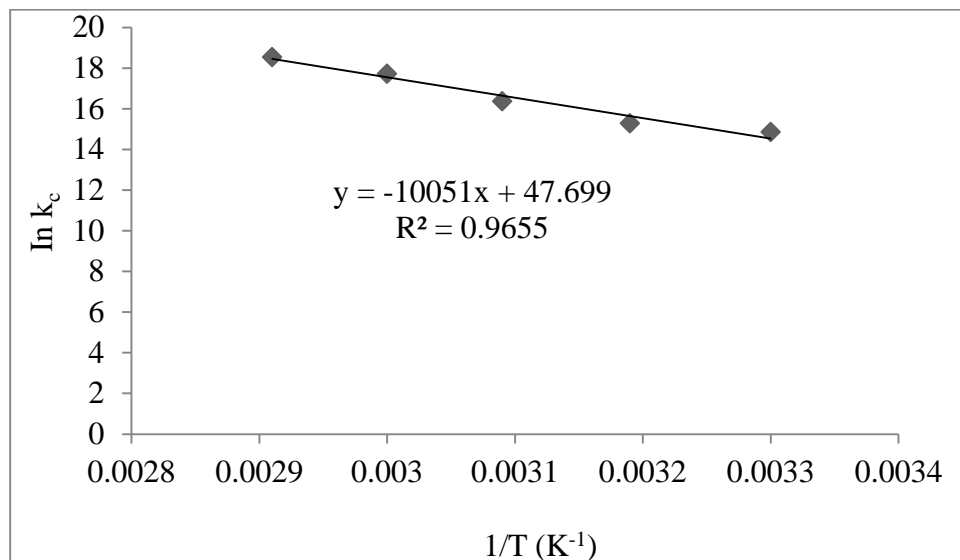
$$k_c = k_L \times 10^6 \quad (6)$$

$$\Delta G^\circ = -RT \ln k_c \quad (7)$$

$$\ln k_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

Where  $k_c$  is the equilibrium constant.

The thermodynamic plot showed a good relationship with correlation coefficient ( $R^2$ ) equal 0.965.



**Fig. 16: Thermodynamic plot for the adsorption of phenol onto OPP**

**Table 8: Thermodynamic parameters of adsorption of phenol onto OPP**

T (K)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (kJ/mol)
303.15			- 36.60
313.15			- 40.60
323.15	83.56	396.49	- 44.60
333.15			- 48.50
343.15			- 52.50

The thermodynamic values of phenol removal using OPP at different temperatures is shown in Table 8. The enthalpy value of adsorption ( $\Delta H^\circ$ ) of phenol – petiole system was found to possess a positive value indicating an endothermic process. The positive value of entropy ( $\Delta S^\circ$ ) indicated that there was an increase in randomness at the solid/solution interface during the removal process. The change in the Gibbs free energy ( $\Delta G^\circ$ ) values of phenol removal using OPP was found to be of negative which indicated that the process was feasible and spontaneous in nature.

### Conclusion

This study has demonstrated the usefulness of oil palm petiole (OPP) as a potential adsorbent for the remediation of phenol impacted aqueous medium. The characterization of OPP using FTIR Spectrophotometer showed that surface functional groups such as carboxylic, amino, and hydroxyl groups at different FTIR bands play important role in phenol removal using OPP biomass. This study has also revealed the bioactive and metal compositions of the OPP which can be useful in other formulations such animal feeds, emulsions, soap, drugs, etc. This study revealed an excellent removal efficiency of 99.91% at optimum pH of 12 and adsorption equilibrium time of 40 minutes.

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