

# Multi Layer and Non Spontaneous Sorption of Chlorpyrifos by Magnetic Responsive Pineapple Crown Leaves Powder

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**Abstract** - In previous studies, pineapple crown leaves powder (PCLP) has been used as the adsorbent for the removal of dyes and metals from water but the application of PCLP in the remediation of pesticides has been overlooked. This study is done to elucidate the role of lignocellulosic materials in the cell wall of PCLP and the impregnated iron oxide in the sorption process of chlorpyrifos in aqueous solution. The pineapple crown leaves powder impregnated with magnetic iron oxide nanoparticles (MPCLP) was synthesized using the co-precipitation method involving ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and sodium hydroxide (NaOH). The raw materials and the prepared adsorbents were characterized by Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray (EDX), surface area (BET- $\text{N}_2$ ), Neutral Fiber Detergent (NDF) and zeta potential analysis. The effect of contact time, adsorbent dosage and pH on chlorpyrifos removal was investigated. Batch sorption studies were conducted to compare the ability of the raw PCLP, acid treated PCLP and the MPCLP for the removal of chlorpyrifos. The removal of chlorpyrifos by adsorption process increased rapidly in the first ten to twenty minutes and became slower gradually after 30 minutes. The adsorption process was pH dependent and greater uptake occurred at pH 8. The increase in chlorpyrifos uptake was related to the increase in adsorbent dosage. The MPCLP was selected to acquire the adsorption isotherm due to its chlorpyrifos removal in batch studies. Equilibrium data fitted better in Freundlich isotherm model ( $R^2 = 0.7760$ ) compared to Langmuir model ( $R^2 = 0.2798$ ) which shows that the adsorption of chlorpyrifos occurred in multilayer adsorption. The apparent kinetic data was represented by the pseudo second order kinetics. Thermodynamic parameters were estimated and the obtained

results concluded that, the chlorpyrifos adsorbed onto MPCLP are non-spontaneous processes. The  $\Delta G^\circ$  for the adsorption of chlorpyrifos was at the highest at 293K (8.47kJ/mol) suggesting that the adsorption favored lower temperature. A negative value of  $\Delta H^\circ$  (-45.77 kJ/mol) suggesting that the reaction is an exothermic process. The negative value of  $\Delta S^\circ$  (-144.65 J/mol/K) indicating that the adsorption of chlorpyrifos onto the adsorbent surface happen in a particular order. As determined by the experimental data, MPCLP has the potential as the alternative adsorbent for the remediation of chlorpyrifos in aqueous system.

**Key Words:** Chlorpyrifos, Pineapple Crown Leaves Powder, Magnetic Sorbent, Multilayer Sorption, Non-Spontaneous Sorption

## 1. INTRODUCTION

Chlorpyrifos has been characterized as moderately toxic insecticides by the World Health Organization (WHO) (1). The half-life of chlorpyrifos in soil is between 10-120 days depending on the environmental factors (2). Despite its short half-life in soil, chlorpyrifos still pose a threat to the non-target organisms because of its ability to disrupt the nervous system by inhibiting the activity of acetylcholinesterase causing weakness or paralysis (3). Accumulation of chlorpyrifos in the environment may cause ecological stress (4) such as being toxic to the variety of arthropods such as bees and may kills fishes and birds even at low concentration (5). Chlorpyrifos can be considered as one of the contaminants of emerging concern (CEC) because when it is mineralized by biodegradation, hydrolysis and photolysis, it become easily become soluble and available in our water system (6).

Prolonged exposure to chlorpyrifos may result in kidney problem to human [(7); (8)]. Chlorpyrifos has been declared as toxic to the genes and may caused human cells mutations (9). Unfortunately, many types of fruits produced by China are loaded with chlorpyrifos because China uses the most pesticides in the world (10). Chlorpyrifos is also commonly found in fruits and vegetables samples imported from Thailand (11).

Chlorpyrifos has the tendency to leach into our water bodies during its application at the plantation area and adsorption technique is considered suitable for the removal of chlorpyrifos in aqueous system (2). Magnetic and mesoporous adsorbent materials such as magnesium ferrite (MgFe<sub>2</sub>O<sub>4</sub>) has showed 99% of chlorpyrifos removal via adsorption process (12). Besides, carbon-based materials such as biochar from sugarcane bagasse has achieved good chlorpyrifos removal of 89% at 20°C (13).

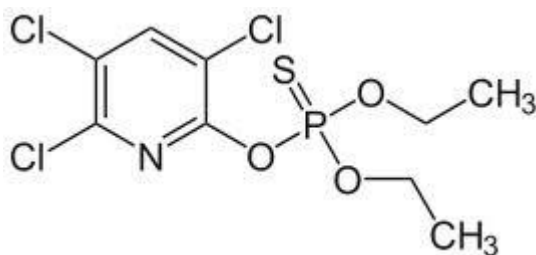


Fig -1: Chemical structure of chlorpyrifos

Pineapple crown leaves poses great characteristic which is suitable for high strength adsorbent production due to its cellulose and hemicelluloses content (14). Due to its good mechanical strength, pineapple leaf fiber has been exploited for the development of alternative sorbent materials as summarized in table 1. Fibers contained in pineapple crown leaves are very suitable to be utilized as sorbent material because it is hydrophilic in nature due to the presence of high cellulose content [(15); (16); (17)]. A reliable adsorbent must exhibit certain characteristics such as high surface area and relatively short contact time to achieve adsorption equilibrium (18).

Table -1: The summary of the utilization of pineapple leaf fiber for the development of sorbent materials.

Sorbents development			
Sorbent	Sorbate	Performance	Reference
Raw pineapple leaves	Rose bengal (dye)	The raw sorbent removed more sorbate compared to the thermally treated sorbent with adsorption capacity of 58.8 mg/g and the adsorption data fit in Freundlich equation.	(19)
Magnetically separable activated carbon from pineapple crown leaves	Zinc (metal ion)	Zinc was removed (70.5%) at pH 4 and the adsorption equilibrium reached after 180 minutes.	(20)
Coupling iminodiacetic acid with the pineapple leaves	Lead (metal ion)	Iminodiacetic acid coupled leaves capable of maintaining its adsorption ability more than 87% after four cycles of adsorption and desorption.	(21)
Cetyltrimethyl ammonium bromide modified pineapple leaves	Paraquat (pesticide)	The sorption data fitted to Freundlich isotherm with multilayer adsorption capacity of 13.0 mg/g.	(22)
Pineapple leaves	Phosphate in laundry waste	Pineapple leaves were treated with 15% HCl and phosphate was highly removed (99.2%) with dosage of 6.0g at phosphate concentration of 2 ppm.	(23)
Pineapple leaves	Chromium (VI) and chromium (III)	Hydroxyl ions were introduced onto the surface of the pineapple leaves and the kinetic data was best described using pseudo-second order.	(24)
Fatty acid esterified pineapple leaves	Dissolved oil	Esterification of pineapple leaves to increase its hydrophobicity and the sorption of followed Langmuir isotherm.	(25)

In general, pretreated cellulosic materials showed higher sorption capability than the untreated materials (26). The acid pretreatment of biomass is currently the most applied method to alter the lignocellulose framework (27). Inorganic acids such as sulfuric acid, hydrochloric acid and nitric acid are usually used for dilute acid pretreatment. [(28); (29)]. Biomass derived sorbent can also play the role of a stabilizer for magnetic iron oxide by capping and stabilized the iron oxide in aqueous solution (30). Lignocellulosic materials that exist in pineapple leaves or other agricultural wastes has a few functional groups that are capable of binding with iron such as hydroxyl and carbonyl (31).

Magnetic iron oxide can be synthesized using chemical co-precipitation and this technique involving the addition of alkali (32). Magnetic iron oxide is usually microscopic and responsive towards magnetic field. Sorbent materials that have been permeated with magnetic iron oxide is it can easily separated from aqueous solution using magnetic separator [(33); (34); (35)].

Therefore, the aim of this study is developing alternative sorbent from pineapple crown leaves that also act as capping agent for the magnetic iron materials. The ability of the developed sorbent will be evaluated by the removal of chlorpyrifos from aqueous systems. The effects of adsorption parameters such as contact time, pH and sorbent dosage and temperature were investigated using three types of adsorbent which were the raw PCLP, acid modified PCLP and magnetized acid treated PCLP (MPCLP). The adsorption isotherms, kinetics and thermodynamic were further studied using MPCLP.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of PCLP

The pineapple crown leaves from Millie Dillard (MD2) variety of pineapple were used as the raw material in this study. The leaves were manually chopped and washed with distilled water to remove the surface-adhered particles and was dried at 70°C overnight. The dried leaves were then grounded and sieved through 0.43-mm mesh size and collected on 0.15-mm mesh to be used for subsequent studies. The dried samples were kept in desiccator before further use.

The PCLP was pretreated with nitric acid, HNO<sub>3</sub> (0.1M and 1.0M) and the effect of this weak acid hydrolysis towards its surface area was studied. The acid treated PCLP were prepared by suspending the PCLP in HNO<sub>3</sub> solution for 24 hours at 37°C in a shaking incubator. After the pretreatment process, the adsorbents were rinsed with deionized water and oven-dried until constant weight.

### 2.2 Preparation of magnetic iron oxide

The magnetic iron oxides were produced by co-precipitation technique by dissolving 0.72g of FeCl<sub>3</sub>.6H<sub>2</sub>O and 0.80g of FeSO<sub>4</sub>.7H<sub>2</sub>O in 52mL and 6mL distilled water respectively as described by (36). Both solutions were then combined and stirred vigorously until the temperature of the mixture reached 70°C. The stirring process was later continued slowly at room temperature for another 30 min. Lastly, 10 M of sodium hydroxide, NaOH solution was added until the pH of the suspension reached pH 11. The solution was then combined with 5 g of PCLP and was aged at room temperature for 24 hours. After the aging process, the iron oxide impregnated PCLP (MPCLP) were cleaned and dried at 70°C for 24 hours and were ready to be used.

### 2.3 Characterization of PCLP and MPCLP

The PCLP and MPCLP were characterized using Energy Dispersive of X-rays (EDX) that was done simultaneously with Scanning Electron Microscopy (SEM) for the determination of chemical composition and surface morphology. The analysis of cellulose, hemicellulose and lignin of the raw PCLP, acid treated PCLP and MPCLP were also determined using Neutral Fiber Detergent (NDF) method. Specific surface area of adsorbent was done using a single-point BET-N<sub>2</sub> (Brunauer, Emmett, Teller) method while the net surface charge of the three sorbents in solution was also analyzed by determining its pH at point of zero charge (pH<sub>zpc</sub>).

### 2.4 Batch adsorption study for the removal of chlorpyrifos

Batch adsorption experiments were conducted to observe the ability of the raw PCLP, acid treated PCLP and MPCLP for the sorption of chlorpyrifos in aqueous solution. A set of batch experiments were done using 250 mL of Erlenmeyer flasks by adding a fixed amount of dry adsorbent with 100 mL of 10 mg/L of chlorpyrifos solution. The analysis was carried out at varying of contact time, pH and dosage of the sorbents. The mixture was shaken in a rotary shaker at 120 rpm followed by filtration using Whatman Grade 1 qualitative filter paper. The filtrate containing the residual concentration of chlorpyrifos was determined using UV-Visible spectroscopy at 450 nm. The parameters studied for adsorption process of chlorpyrifos is shown in Table 2.

**Table -2:** Parameters for adsorption study

Parameters	Analysis range	Unit
Contact time	0-60	minute
Sorbent dosage	0.1- 1.0	gram
pH	2 - 12	-

### 2.5 Preparation of chlorpyrifos solution

For the analysis of chlorpyrifos, the standard was purchased from Merck. The chemical structure of chlorpyrifos is given in Figure 1(a). Stock solution of chlorpyrifos (1000 mg/L) was prepared in acetonitrile purchased from Merck and a few working solutions at different concentrations were prepared by diluting the stock solution with distilled water and stored at 4°C.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Lignocellulosic content and surface areas of raw PCLP, acid treated PCLP and MPCLP

The physical appearance of the raw PCLP was in brownish color due to the presence of lignin and hemicellulose as shown in Figure 2 (a) [(38); (39)]. After the pretreatment with HNO<sub>3</sub>, the color of the fiber of PCLP became lighter due to the elimination of lignin and hemicellulose in Figure 2 (b). The same finding was also reported by Mamani et al (39) after the pineapple crown underwent acid washing process. The PCLP used in this study has low lignin content because MD2 pineapple variety is categorized under non-wood fibers that normally contains small amount of lignin (14).

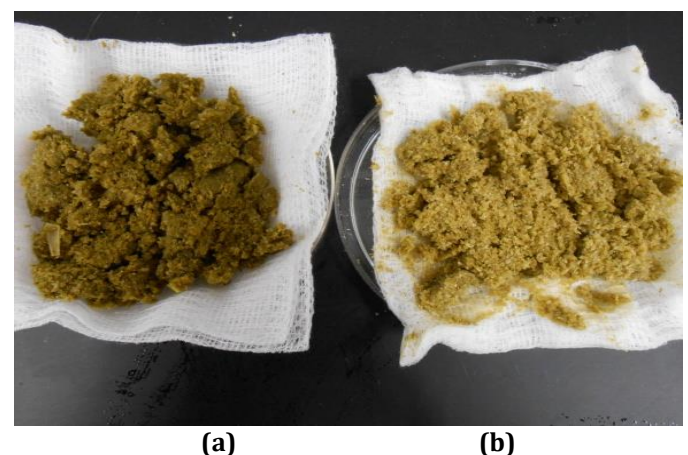
The composition of lignocellulosic materials in PCLP is shown in Table 3. The PCLP comprised of more cellulose, hemicellulose and lignin before the acid hydrolysis. The composition of the fiber is unique depending on the species of the plant, the age of the plant and also the conditions it is planted (40). After the acid hydrolysis, the percentage of hemicellulose was reduced significantly from 78.1% to 53.8%. This result was in line with earlier researches that analyzed the composition of fiber in pineapple crown leaves after acid pretreatment process [(38); (39);(41); (42)].

Lignocellulosic materials in PCLP that has been pretreated with 1.0M HNO<sub>3</sub> was chosen to be incorporated with magnetic nanoparticles via co-precipitation technique involving the solution of combined FeCl<sub>3</sub>.6H<sub>2</sub>O and FeSO<sub>4</sub>.7H<sub>2</sub>O in alkaline condition. After the modification of PCLP, the magnetized PCLP (MPCLP) could be easily separated using the magnetic separators. The specific surface

area of PCLP before the modification was 18.1 m<sup>2</sup>/g while the surface area for MPCLP was 32.0 m<sup>2</sup>/g as shown in Table 3.

**Table -3:** Effect of different concentration of HNO<sub>3</sub> on the surface area and lignocellulosic composition of PCLP

Lignocellulosic content and surface area	Raw PCLP	PCLP (0.1M HNO <sub>3</sub> )	MPCLP
Lignin (%)	12.5	10.8	9.5
Cellulose (%)	51.4	45.1	41.8
Hemicellulose (%)	83.1	78.1	53.8
Surface area (m <sup>2</sup> /g)	6.5	18.1	32.0

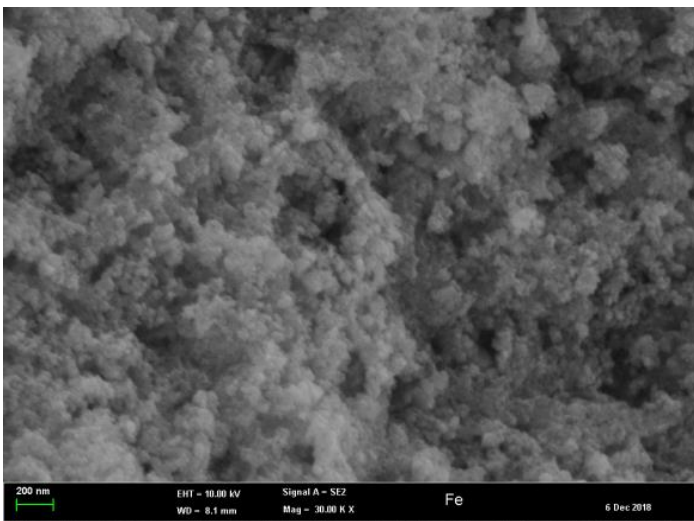


**Fig -2:** (a) The physical appearance of raw, ground and dried raw PCLP (b) PCLP after acid pretreatment

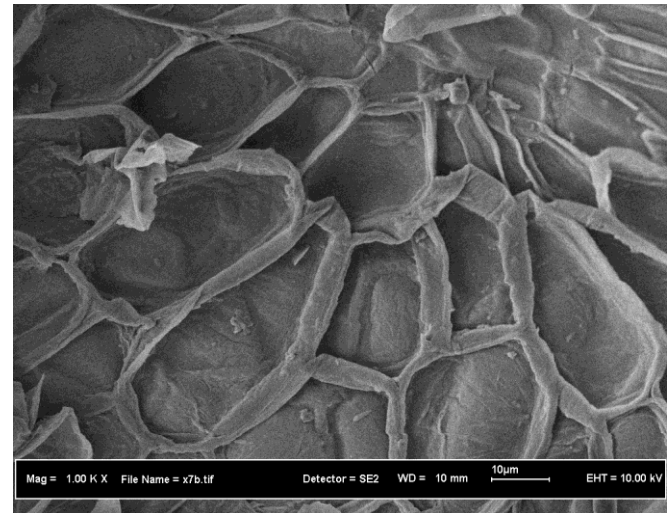
### 3.2 Scanning Electron Microscope Images (SEM) and Energy Dispersive of X-rays (EDX)

#### 3.2.1 SEM micrograph and EDX analysis of synthesized iron oxide

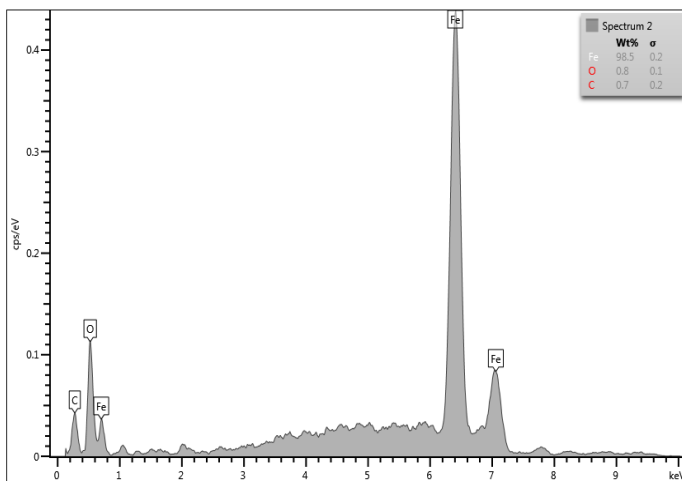
The iron oxide has been successfully synthesized via co-precipitation technique. The SEM micrograph revealed the surface morphology of the synthesized iron oxide that consisted of particles with uniform size with almost spherical shape (Figure 3a) and from the EDX analysis, it was confirmed that the iron is the main element in the sample (Figure 3b). For newly synthesized iron oxide, the iron content was higher (98.2%) than the oxygen (0.8%) and carbon (0.7%) which indicates a pure iron oxide nanoparticle.



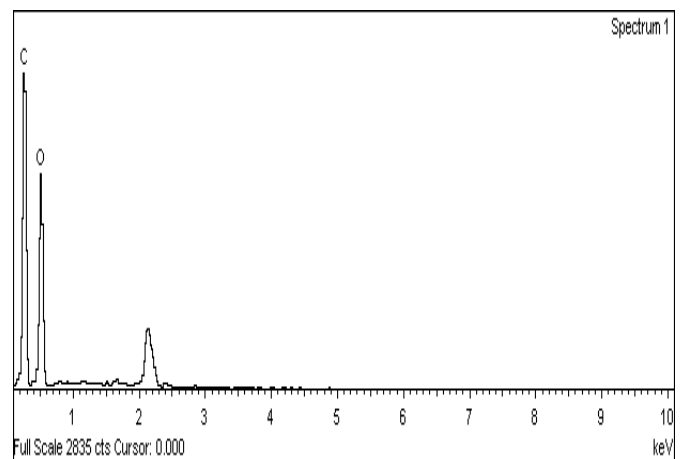
**Fig -3 (a):** Surface morphology of iron oxide at 30,000x magnification



**Fig -4 (a):** Surface morphology of the raw PCLP at 1000x magnification



**Fig -3 (b):** Elemental analysis of iron oxide obtained from EDX



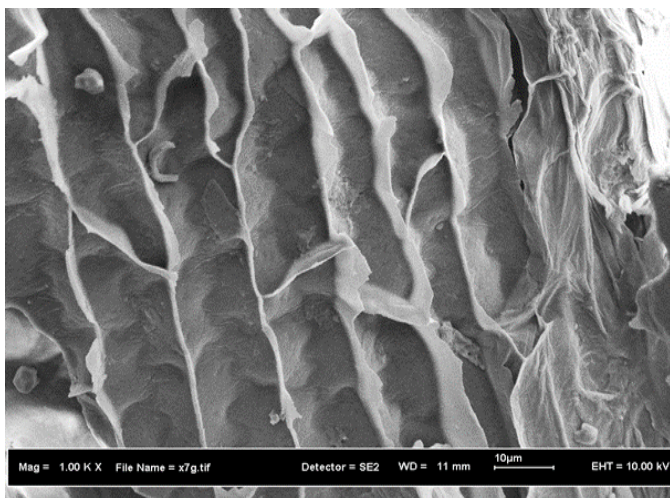
**Fig -4 (b):** Elemental analysis of the raw PCLP obtained from EDX

### 3.2.2 The SEM micrograph and EDX analysis of raw PCLP

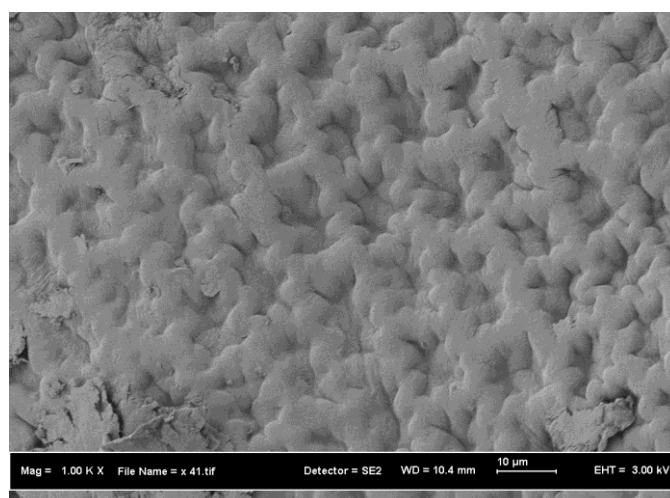
The morphological analysis was carried out to observe the surface changes of the developed sorbent. The surface structure of the raw PCLP is shown in Figure 4 (a) and the elemental composition of the raw PCLP is shown in Figure 4 (b). Based on Figure 4(a), it is evident that the fiber that form pineapple crown leaves are multicellular and the cells arrangement were closely compacted (43). For the EDX results of the raw PCLP, the carbon content was found to be higher (59.78%) as compared to oxygen (40.22%). The higher percentage of carbon may be attributed to the lignocellulosic materials, while oxygen probably obtained from the hydroxyl groups.

### 3.2.3 SEM micrograph of acid treated PCLP

After being pretreated with acid, the raw PCLP showed roughness with no clear cell wall shape as the result of acid hydrolysis that removes certain amount of hemicellulose and lignin as shown in Figure 5 (a). Similar findings was observed for the effect of chemical pretreatment on the surface of pineapple leaf fiber (44)



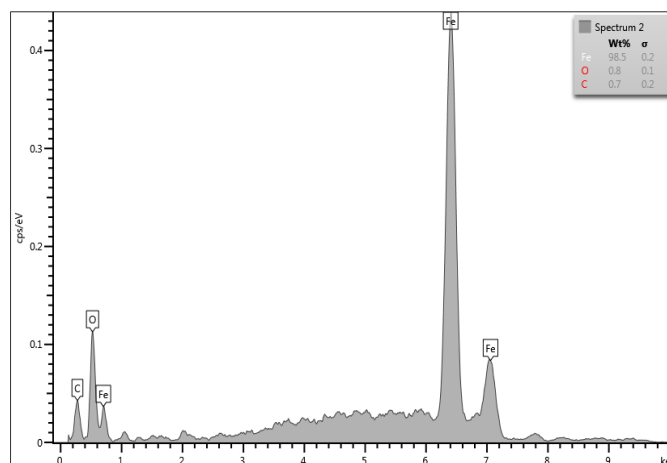
**Fig -5 (a):** Surface morphology of the acid treated PCLP at 1000x magnification



**Fig -6 (a):** Surface morphology of the MPCLP at 1000x magnification

### 3.2.4 SEM micrograph and EDX analysis of MPCLP

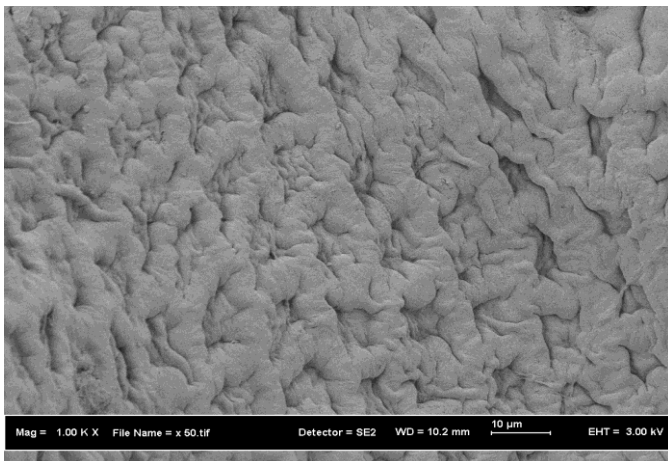
In this research, the magnetic iron oxide was synthesized at ambient temperature in highly alkaline aqueous system that has causes swelling of the cellulose structure in Figure 6 (a). Previous research has concluded that hydrated alkali ions that was present in aqueous system together with lignocellulosic materials will cause the swelling of the cellulose structure by slipping into the cell wall of the lignocellulosic sorbent and the combination of water solvation shell with the OH groups from the cellulose. This phenomenon is also known as mercerization and this will induce the reactivity of the lignocellulosic materials in PCLP to aqueous chemicals due to the increase of surface area (45). Kleinschek *et al*, (45) was also suggesting that, in alkaline condition the fibrilla structure of any lignocellulosic material is loosened and the swelling process occurred as well as the accessibility of active groups on its surface will be increased. Elemental analysis of acid treated pineapple leaf powder impregnated with iron oxide showed the composition of carbon, oxygen, and iron. Percentage of iron may be achieved from iron oxide impregnation. Hence, based from this EDX analysis, it clearly shown the iron oxide was successfully impregnated.



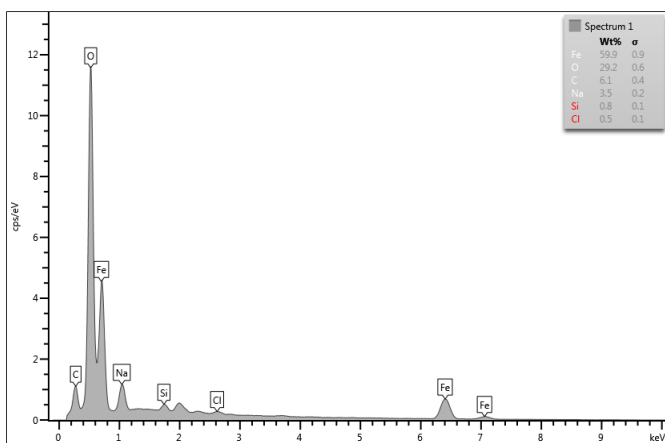
**Fig -6 (b):** Elemental analysis of MPCLP obtained from EDX

### 3.2.5 SEM micrograph and EDX analysis of MPCLP after the sorption of chlorpyrifos

The lignocellulosic materials became more saturated and swollen in MPCLP after the sorption of chlorpyrifos as shown in Figure 7 (a). The sorption of chlorpyrifos can be proven by the detection of chlorinated substance from the EDX analysis as shown in Figure 7 (b). After the adsorption process, the EDX analysis showed the percentages of these elements 59.9% iron, 29.2% oxygen, 6.1% carbon and 0.5% chlorine.



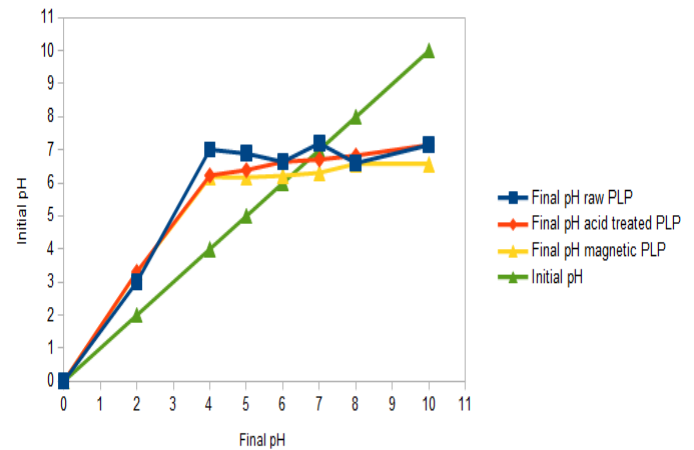
**Fig -7 (a):** Surface morphology of the MPCLP after the sorption of chlorpyrifos at 1000x magnification



**Fig -7 (b):** Elemental analysis of MPCLP after the sorption of chlorpyrifos obtained by EDX

### 3.3 The pH at zero point of charge (pH<sub>zpc</sub>)

In principle, pH<sub>zpc</sub> is used to explain the possible interaction and repulsion information between the sorbent and the sorbate (46). The experiment of pH<sub>zpc</sub> was carried out to determine the pH when the surface charge of the sorbents was zero. The pH<sub>zpc</sub> of raw PCLP, acid treated PCLP and magnetic PCLP were 7.2, 6.7 and 6.2 respectively (Figure 8). At pH higher than pH<sub>zpc</sub>, the surface of the sorbent become negatively charged and can associate with positive species while pH lower than pH<sub>zpc</sub> the sorbent surface will be positively charged and attract negative species [(46); (47)]. In this study, chlorpyrifos has pKa value of 4.55 and from the pH<sub>zpc</sub> results it can be predicted that chlorpyrifos can be removed at higher pH values when the sorbent's surface is



negatively charged. Neupane and co-workers (48) reported that pH<sub>zpc</sub> of the untreated PCLP for the removal of crystal violet was 6.0. The untreated PCLP that being used as sorbent for copper removal showed pH<sub>zpc</sub> value of 2.3 (49).

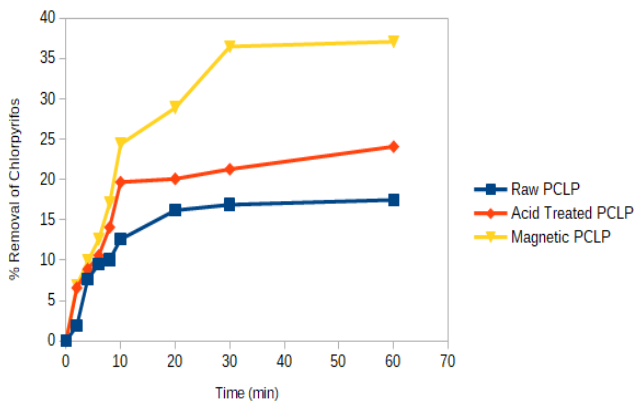
**Fig -8:** The comparison of the pH<sub>zpc</sub> of raw PCLP, acid treated PCLP and MPCLP

### 3.5 Comparison study on the factors affecting the sorption of chlorpyrifos by raw PCLP, acid treated PCLP and MPCLP

The batch or static system were carried out by adding certain amount of sorbents into chlorpyrifos solution and the experimental mixtures were shaken at certain reaction time before the final concentration chlorpyrifos was analyzed.

#### 3.5.1 Effect of contact time

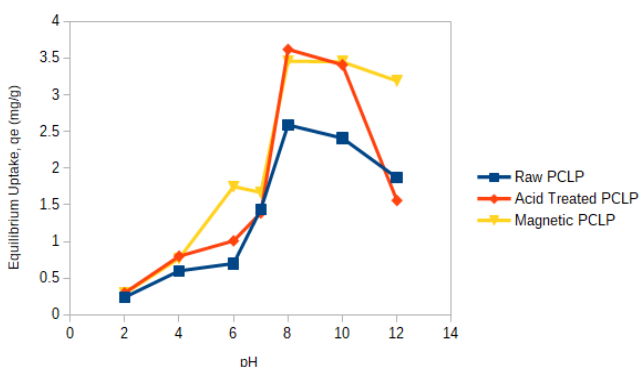
Chlorpyrifos was sorbed rapidly by all three types of sorbent during the first 10 minutes of contact time as shown in Figure 9. The removal became slower until contact time reached 30 minutes possibly due to the saturation of sorption sites on the surface of sorbents. No significant removal was observed after 30 minutes to 60 minutes of contact and this clearly showed that equilibrium was achieved at 30 minutes of contact time.



**Fig -9:**The comparison of percentage removal of chlorpyrifos in aqueous batch system by raw PCLP, acid treated PCLP and magnetic PCLP at different contact time

### 3.5.2 Effect of pH

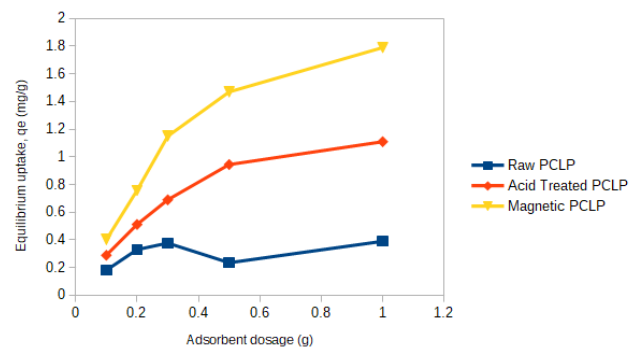
It is notable that pH will influence the ionization of active sites on the sorbent material (46). The effect of the variation of pH values (pH 2-12) in the sorption of chlorpyrifos can be observed in Figure 10. The sorption of chlorpyrifos was pH dependent because chlorpyrifos has a pKa value of 4.55 and can be easily sorbed onto negatively charged sorbent. From Figure 11 the equilibrium uptake of chlorpyrifos was higher at higher pH. Maximum uptake was achieved at pH 8 for all sorbent showing MPCLP has the highest uptake. The sorption decreased after pH 8. This probably due to the decomposition of chlorpyrifos to form its by-product known as 3,5,6-trichloro-2-pyridoinol (TCP) at higher pH as reported by El Bouraie et al (50).



**Fig -10:** The comparison of the chlorpyrifos uptake in aqueous batch system by raw PCLP, acid treated PCLP and magnetic PCLP at different pH.

### 3.5.3 Effect of sorbent dosage

The increase amount of all types of sorbents may lead to the increase of chlorpyrifos uptake as shown in Figure 10. This may due to the availability of sorption sites on the surface of sorbents in the experimental solution. The sharp increase in chlorpyrifos uptake for acid treated PCLP and magnetic PCLP was possibly because of the pretreatment that has been applied before the experiment that may increase the ability of the sorbent to capture more chlorpyrifos compared to the raw PLP. During the acid treatment, the surface of PCLP was ruptured and became flaky to increase its surface area. The surface of acid treated PCLP was then became swollen after being exposed to high concentration of NaOH causing the surface area to increase.



**Fig -11:** The comparison of the chlorpyrifos uptake in aqueous batch system by raw PCLP, acid treated PCLP and magnetic PCLP using different amount of dosage.

### 3.5 Study of Adsorption Isotherms

Adsorption isotherms will represent the synergy between adsorbates and adsorbents during adsorption process. Langmuir and Freundlich isotherms are the most used isotherms to understand the process of adsorption. In the present adsorption experiment, the MPCLP has been selected to derive the adsorption isotherm due to its performance in parametric influence studies compared to the other parent adsorbents.



### 3.5.1 Langmuir Adsorption Isotherm

The Langmuir isotherm presumes that the adsorption of chlorpyrifos will happen on a homogenous monolayer surface and the energy of the interaction between the adsorption sites and the adsorbates is identical (51). The Langmuir equation in the linear form can be written as

$$C/q_e = (1/Q_o K) + (C/Q_o)$$

where C is the equilibrium concentration of chlorpyrifos in solutions (mg/L),  $q_e$  is the maximum uptake amount per g of adsorbent (mg/g), and K is the Langmuir constant related to binding energy of the sorption system (L/mg). In this study the first Langmuir isotherm equation was selected and the Langmuir parameters,  $Q_o$  and K can be obtained from the linear plot of  $C/q_e$  against C in Figure 12. The values of parameters were calculated and shown in Table 4.

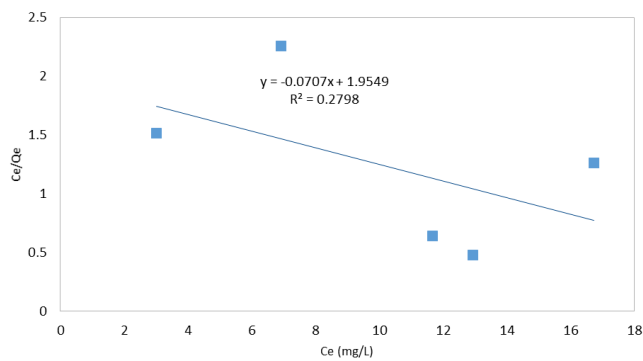


Fig -12 : Langmuir adsorption isotherm for the removal of chlorpyrifos by MPCLP

### 3.5.2 Freundlich Adsorption Isotherm

Freundlich adsorption isotherm indicates that adsorption happens on a heterogeneous surface with non-uniform adsorption energies generated during the process (52). The linearized form of the Freundlich equation can be described as follows:

$$q_e = KCe^{1/n}$$

$$\log q_e = \log K + (1/n)\log C_e$$

where K is the Freundlich constant describing the adsorption capacity while 1/n is a constant describing the adsorption intensity (53). The smaller the value of 1/n will result in stronger adsorption binding between adsorbent and adsorbate (54). The plot of  $\log q_e$  against

$\log C_e$  is shown in Figure 13. The values of parameters were calculated and also tabulated in Table 4.

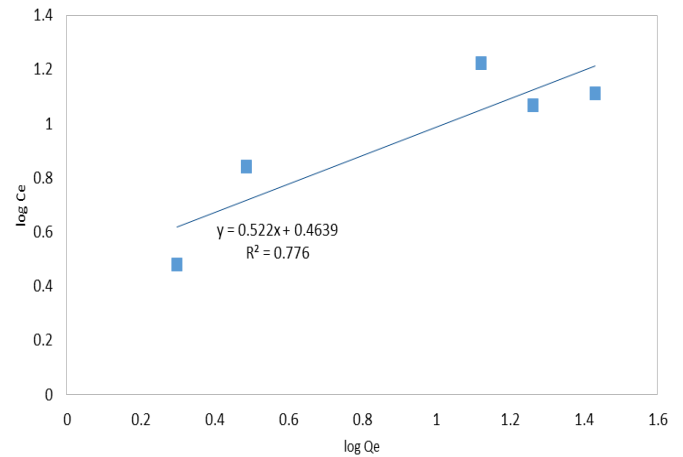


Fig -13: Freundlich adsorption isotherm for the removal of chlorpyrifos by MPCLP

Table-4: Isotherm parameters for the adsorption of Chlorpyrifos by MPCLP

Langmuir Isotherm Model			Freundlich Isotherm Model		
$K_a$ (L/mg)	$Q_m$ (mg/g)	$R^2$	$K_F$	1/n	$R^2$
-0.0362	-14.1443	0.2798	2.911	0.5220	0.7760

### 3.6 Kinetic Study

Kinetic study is important as it provides an understanding on the mechanism of adsorption (either physical or chemical reaction) that happens between the adsorbent and adsorbate in a system (55). In batch adsorption study, a few kinetic models can be implied such as pseudo-first-order and pseudo-second-order models.

To determine the chlorpyrifos adsorption kinetic, the batch study data were fitted to equation  $\ln(q_e - q_t) = \ln q_e - K_1 t / 2.303$  for pseudo-first order and  $t/q_t = 1/(K_2 q_e^2) + 1/q_e$  for pseudo-second-order, where  $q_t$  is the amount of chlorpyrifos adsorbed at time, t and  $K_1$  and  $K_2$  ( $\text{min}^{-1}$ ) are pseudo-first order and pseudo-second-order constants respectively.

Chlorpyrifos adsorption resulted to be better modeled by pseudo-second-order kinetic equation as shown in Table 5. Moreover,  $R^2$  that measures the accuracy of the data was higher in pseudo-second-order linear plot indicating better connection between the theory of kinetic and the experimental data obtained (56).

**Table-5:** Kinetics parameters for the adsorption of chlorpyrifos by MPCLP

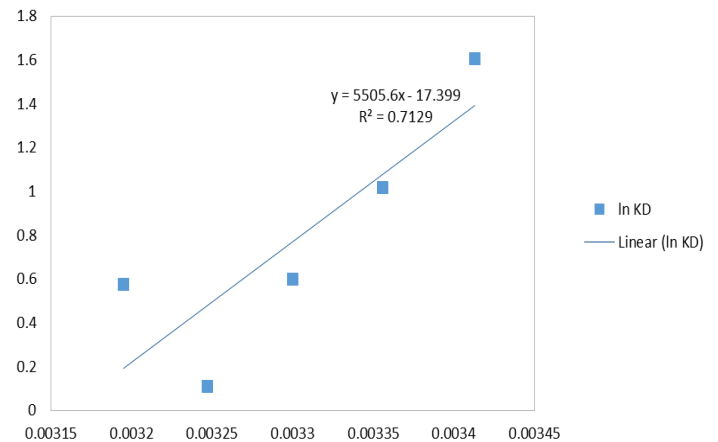
Pseudo-first-order Model				Pseudo-second-order Model			
$Q_e$ (mg/g)	$Q_e$ (cal)	$K_1$	$R^2$	$Q_e$ (cal)	$K_2$	$h$	$R^2$
4.95	0.288	0.048	0.443	3.26	0.017	0.185	0.797

### 3.7 Thermodynamic study

Thermodynamic study can predict the spontaneous nature of the adsorption phenomenon. Thermodynamic study of chlorpyrifos adsorption was conducted at 293K, 298K, 303K, 308K and 313K. The effect of these temperatures on chlorpyrifos adsorption can be predicted using Gibbs free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ). Linear plot of  $\ln K_D$  against  $1/T$  was plotted as shown in Figure 14. The values for  $\Delta H$  and  $\Delta S$  can be obtained from the slope and intercept of Van't Hoff linear plot in this equation ;  $\ln K_D = (\Delta S^\circ/R) - (\Delta H^\circ/ RT)$  where  $K_D$  is distribution coefficient,  $R$  is gas constant ( $8.314\text{J K}^{-1} \text{mol}^{-1}$ ) and  $T$  is temperature (K). Distribution coefficient,  $K_D$  can be calculated by using this equation;  $K_D = C_e/q_e$ , where  $C_e$  is the concentration of chlorpyrifos in solution (mg/L) and  $q_e$  is equilibrium uptake (mg/g).

From Table 6, Gibbs energy values of the adsorption of chlorpyrifos was the highest when the adsorption occurred at 293K. At this temperature it can be concluded that the intermolecular forces between chlorpyrifos and the adsorbent was high. The value of  $\Delta G^\circ$  became lower at 298K but there was a slight increase in Gibbs energy values when the temperature increase from 298K to 313K suggesting that adsorption of chlorpyrifos was more favourable at lower temperature. The positive values of Gibbs energy indicating that the adsorption of chlorpyrifos that occur at this range of temperature was a non-spontaneous process. A negative value of  $\Delta H^\circ$  indicating that the reaction is exothermic in nature. The negative value of

$\Delta S^\circ$  suggesting that the adsorption of chlorpyrifos onto the adsorbent surface happen in a particular order (57).



**Fig -14:** A plot of  $\ln K_D$  against  $1/T$  for chlorpyrifos removal by MPCLP at different temperatures

**Table-6:** Thermodynamic parameters for adsorption of chlorpyrifos from aqueous solution by MPCLP

Thermodynamic parameters							
$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol/K)	$R^2$	$\Delta G^\circ$ (kJ/mol)				
			293 K	298 K	303 K	308 K	313 K
-45.77	-144.65	0.71	8.47	4.31	4.38	4.45	4.52

### 4.0 CONCLUSION

The sorption of chlorpyrifos from aqueous solution by the raw PCLP, acid treated PCLP and MPLP has been investigated under different experimental conditions in batch mode. The removal of chlorpyrifos occurred rapidly at the first 10 minutes of contact time and started to reach equilibrium when the reaction time reached 30 minutes. The uptake of chlorpyrifos was also affected by the amount of sorbent used. The uptake increased when more sorption sites available in the system. The sorption was also pH dependent since chlorpyrifos with pKa 4.55 is more easily sorbed onto negatively charged sorbents. The equilibrium data of the ability of MPCL to remove chlorpyrifos could be well interpreted by Freundlich isotherm. The results demonstrated that the adsorption of chlorpyrifos happened on multilayer. From the thermodynamic study, the adsorption of chlorpyrifos by MPCLP was exothermic in

nature suggesting that adsorption become easier at lower temperature and the adsorption happen non-spontaneously.

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