

# IMPROVED REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTION USING NaOH-PRETREATED COCO PEAT

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## ABSTRACT

This study aims to analyze the effect of chemical pretreatment using sodium hydroxide (NaOH) on the capacity of coco peat in removing of copper (II) ions from aqueous solutions. The effects of varying the molarity of NaOH, the solution pH, initial Cu(II) concentration, coco peat dosage and contact time were studied in batch experiment. The result of the preliminary pretreatment study shows that treatment with 0.5M NaOH greatly enhanced the metal sorption capacity of raw coco peat. The uptake capacity for Cu of the raw coco peat was increased from 46% to 83% at pH 4.0 and from 15% to 27% uptake for initial solution pH of 2.4. The results showed that the removal rate is directly proportional to pH, coco peat's dosage and contact time and inversely proportional to Cu(II) concentration. The adsorption process is best explained by the Langmuir isotherm than the Freundlich isotherm, indicating monolayer adsorption on a homogenous surface. The rate of reaction follows the pseudo-second order kinetic model, signifying that chemisorption is the rate-limiting mechanism. The results of the Fourier Transform Infra-Red (FTIR) analysis indicated that the main functional groups involved in the sorption of copper to NaOH pretreated coco peat are the hydroxyl, carboxyl and phenolic groups. Based on the results of this study, it was found that pretreating coco peat with NaOH significantly improve the overall efficiency of coco peat in removing Cu(II) by adsorption process.

**Keywords:** Adsorption, Biosorption, Coco peat, Copper ions, Langmuir isotherm, Sodium hydroxide pretreatment

## Introduction

Nowadays, water pollution concerning heavy metals has become one of the major problems we encounter in our environment. One of the main causes of this problem is the improper disposal of wastewater from different industries. Industries like mining and metal plating largely contribute to the high concentrations of heavy metals, such as zinc, cadmium and copper, in our surface waters.

Removing or reducing large amount of heavy metals from wastewater is needed to prevent heavy metal pollution in water and risks to human health. There are several conventional methods of removing/reducing heavy metals from wastewaters, including chemical precipitation, reverse osmosis, filtration, ion exchange, and activated carbon adsorption. However, these processes are usually not feasible and difficult to apply in most settings due to limitations of economic and technical viability.

One promising and low-cost technology for removal of heavy metals in wastewater is biosorption. Biosorption is considered a good alternative to conventional methods because it makes use of readily available biosorbents like fruit peelings, fibers, peat, rice hulls and other agricultural waste, which make the process low-cost. Furthermore, several chemical and physical pre-treatments or modification techniques can also be done to improve the sorption properties of a sorbent, like its removal capacity. Recently, Wan Ngah and Hanafiah [5] extensively reviewed several kinds of low-cost and chemically treated

adsorbents used in removing different heavy metals from aqueous solutions. The review concluded that most of the treated adsorbents like weed, rice husk, saw dust and spent grain showed improved sorption capacities compared to the raw sorbents for heavy metals such as cadmium, copper, lead, nickel and zinc.

In this study, coco peat, which is also called coconut coir or coir fibers, was used as sorbent material to remove of Cu(II) ions from aqueous solution. Coco peat is the material found between the outer coating of a coconut and its hard, inner shell. It is biodegradable but takes as long as 20 years to decompose. It is very abundant in the Philippines and is generally considered a nuisance with little beneficial use and has disposal problem.

Like most biosorbents, coco peat is composed mainly of lignin, cellulose, hemicellulose, pectin, and extractives [4]. It has already been established, through numerous researches, that with the given the properties of coco peat, it is an effective biosorbent in removing heavy metals from wastewaters.

However, until now, adsorption studies involving coco peat in the Philippines have been mainly concentrated on the removal of single and binary species heavy metals such as Pb, Zn Cu, and Cd using just raw or untreated coco peat. Similar studies have shown that affinity of Cu(II) on raw coco peat is lesser compared to other heavy metals, indicating low adsorption capacity [4].

To improve the adsorption capacity for Cu(II), raw coco peat was pretreated with sodium hydroxide (NaOH). Studies prove that chemically pretreating most biosorbents using NaOH would result in the highest removal capacity over the raw biomass and other different chemical pretreatments [7,9]. For instance, Kumar and Bandyopadhyay [2] has reported that pre-treating rice husk using NaOH would give higher Cd(II) uptake capacity as compared to raw, sodium carbonate-treated and epichlorohydrin-treated rice husk.

In this study, the effect of NaOH pretreatment on the adsorption capacity of raw coco peat with Cu(II) in aqueous solution has been investigated through equilibrium and kinetic studies. The effect of pH, initial concentration, coco peat dosage and contact time on the adsorption of Cu(II) on NaOH-pretreated coco peat has been also studied using batch experiment. Using Fourier Transform Infra-Red (FTIR) Analysis, the main functional groups involved in the biosorption of Cu(II) on the pretreated coco peat has been identified.

## **Methodology**

### **Materials**

Fresh coco peat was taken from the Soriano Integrated Fiber Corporation in Sariaya, Quezon and was rinsed repeatedly with distilled water to remove small dust and other soluble materials. The washed material was air-dried for several weeks and was then passed through sieve no. 10 to obtain a diameter of less than or equal to 2mm. The sorbent obtained was designated as the raw coco peat.

For tests with varying pH, the acidity of Cu(II) solution was adjusted by addition of drops of 0.1M hydrochloric acid (HCl) and 0.1M NaOH solutions. The pH of the solution was measured using Milwaukee pH600 pH-meter. The Cu(II) concentrations were measured using a V-2000 multi-analyte photometer (CHEMetrics). The measurement of Cu(II) uses copper vacu-vials which employs bathocuproine chemistry [11]. In a neutral solution, copper ions react with bathocuproine to form an orange colored chelate in direct proportion to the copper concentration.

## **NaOH Pretreatment on Coco Peat**

Coco peat was mixed with NaOH solution in a beaker and stirred using a magnetic stirrer at 150 rpm for 4 hours. The mixture was then filtered. The soaked coco peat was washed several times with distilled water until a neutral pH was reached, to be certain that all the NaOH was almost removed [7]. The materials were air dried for 2 weeks and were designated as NaOH-treated coco peat.

## **Batch Sorption Studies**

To study the effect of NaOH-pretreatment on the sorption capacity of raw coco peat in removing Cu(II) from aqueous solution, 0.1g of NaOH-treated coco peat was mixed in 100 mL solutions with 50ppm Cu(II) concentration. The mixtures were agitated using an orbital shaker (Stuart SSL1) at 150 rpm for 200 mins at room temperature. The samples were then allowed to settle and were filtered. The Cu(II) concentration of the filtrates were measured using photometer (Chemetrics V2000).

Sorption kinetics and the effect of pH on coco peat adsorption capacity were studied using varying contact times of 5, 10, 20, 30, 60, 120 and 200 mins with 0.1g of treated coco peat at pH 2.4 and 4.0.

Isotherm studies were conducted with varying initial Cu(II) concentrations of 10, 20, 30, 50 and 100 ppm. The effect of coco peat dosage on the removal of Cu(II) was also examined using varying coco peat dosages of 0.05, 0.1, 0.15 and 0.2g at pH 4.0 and 200 mins contact time. All batch experiments were conducted in triplicates at laboratory temperature (20°C).

## **Fourier Transform Infra-Red (FTIR) Analysis**

In order to have an idea of the effect of NaOH-pretreatment and Cu(II) uptake to the functional groups present in the samples, a Fourier transform infrared (FTIR) analysis was performed. Several samples were sent to the laboratory for the analysis: raw coco peat, 0.5M NaOH pretreated coco peat, 0.5M NaOH pretreated coco peat contaminated at pH 2.4 and at pH 4. For the contaminated samples, the contact time during adsorption was 200 minutes and the initial Cu(II) concentration of the solution was 50 ppm.

## **Results and Discussion**

### **Effect of Pretreatment**

The effect of pretreating coco peat with NaOH on the sorption of Cu is presented in Figure 1. In order to obtain optimum molarities for the sorption of copper ions, preliminary studies using 0.3M, 0.5M and 0.7M NaOH-pretreated coco peat were done. It was observed that treating the coco peat with 0.5M NaOH aqueous solution for 4 hours would result to the highest removal rate, similar to the result of Low [3].

Treatment with 0.5M NaOH greatly improved the metal sorption capacity of the coco peat at pH 4.0 from 46% to 83% uptake and at initial solution pH of 2.4 from 15% to 27% uptake. The result of this study is consistent with the result of the study of Kumar and Bandyopadhyay [2] with regards to NaOH treatment.

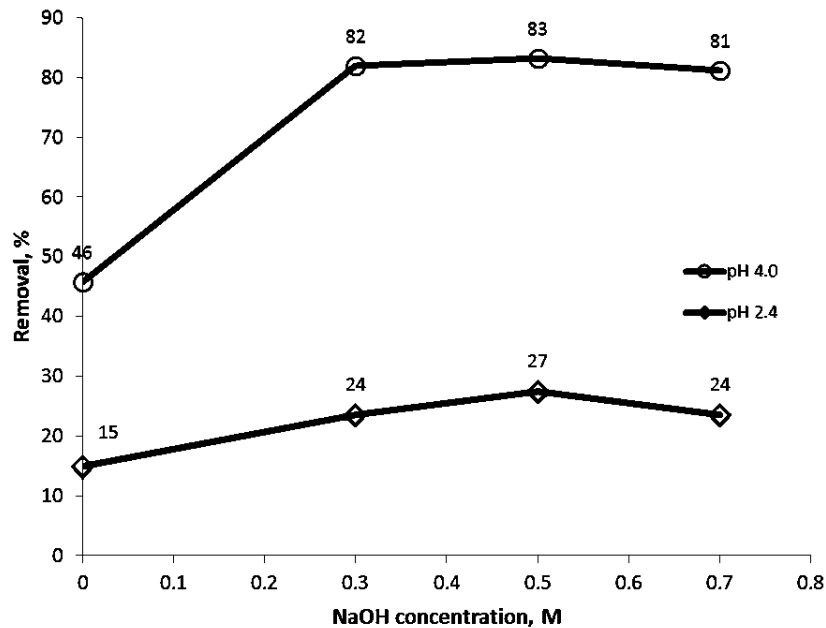


Figure 1. Cu (II) percent removal at varying treatment concentration

A review of related studies revealed that alkali pretreatment significantly enhances the adsorption capacity of raw biomass. The increase in the copper removal capacity after pretreating the coco peat could be explained by the increase of the surface area of the coco peat during the NaOH pretreatment [5]. Also, according to Yan and Viraraghavan [6] and Wan Ngah [5], the increase in the sorption capacity could be due to the removal of base soluble materials and other materials on the coco peat's surface such as lipids, proteins and polysaccharides that may interfere with the adsorption process.

### Effect of Solution's pH and Contact Time

The metal sorption process is generally considered pH-dependent. As shown in Figure 2, there is a direct effect to the amount of copper adsorbed by the NaOH pretreated coco peat upon varying the initial pH of the copper solution. The pH values used in this study were below the 5.5-5.7 pH values for which soluble Cu(II) ions begin to precipitate as metal hydroxide, in which case true adsorption study would be impossible.

It was observed that the optimum pH corresponding to the maximum biosorption of Cu(II) was 4.0. There is a significant increase in the removal rate after the pH is increased from 2.4 to 4.0. This is caused by the decrease in competing ions which results to the increase in the interaction between Cu(II) ions and the binding sites. Acidic solutions contain many free  $H^+$  ions which compete with Cu(II) ions in binding to the coco peat. This means that the more acidic the solution is, the more  $H^+$  ions compete with Cu(II) ions for the binding site, and less sites are left for Cu(II) ions to bind to. This is further supported by the increase in pH of the solution after the adsorption process, caused by the decrease in  $H^+$  ions which are adsorbed by the coco peat.

The rate of sorption of copper for NaOH pretreated coco peat for pH 4.0 and 2.4 are also shown in Figure 2. The initial uptake of copper-ions is very rapid (within 5-30 minutes) followed by a subsequent slow uptake from 30-200 minutes. The process reached equilibrium approximately after 120 minutes. After this time, the amount of adsorbed copper ions was almost constant.

### Effect of Adsorbent Dosage

The effect of coco peat dose on the sorption of Cu(II) was investigated by varying the coco peat amounts from 0.05 to 0.2g. For all these runs, initial Cu(II) concentration was fixed to 50ppm. It is expected that the removal capacity of coco peat would increase with increasing dosage, as shown in Figure 3, because additional adsorbent means additional sites where copper ions can bind to. The maximum removal was obtained in the adsorbent dose of 0.15-0.2g.

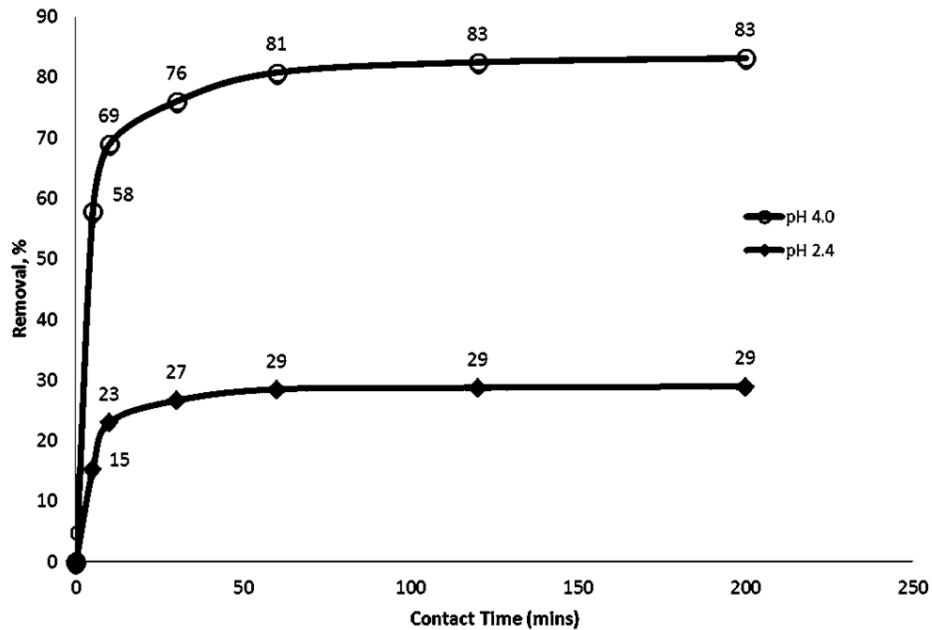


Figure 2. Cu (II) percent removal at varying pH and contact time

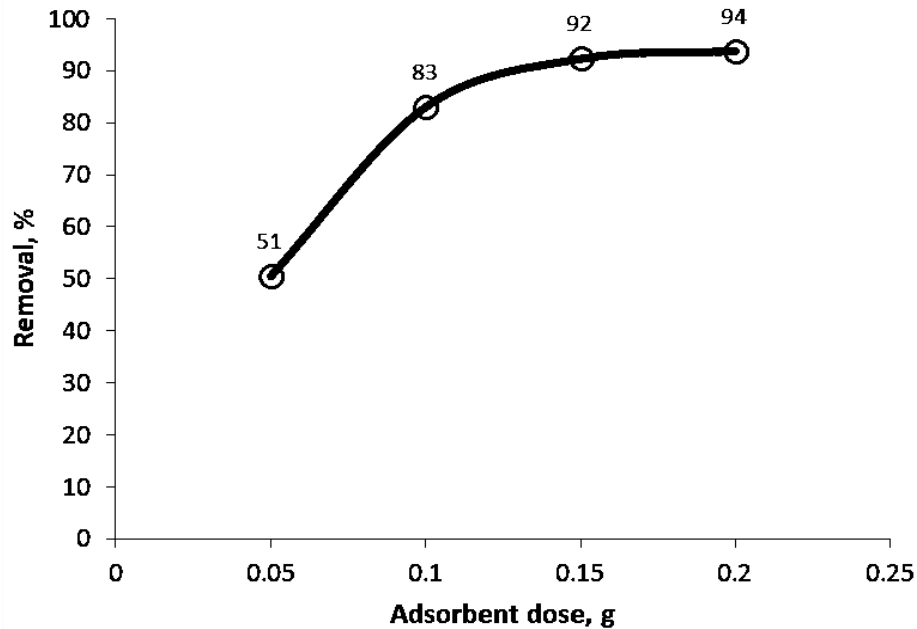


Figure 3. Cu(II) Percent removal at varying adsorbent dose

## Effect of Solution Cu(II) Concentration

The biosorption capacity of the coco peat is also affected by the initial metal concentration to be removed. As shown in Figure 4, the removal rate decreases as the initial concentration of Cu(II) in the solution increases. Higher removal rate is observed at low initial concentrations. The decrease in the removal efficiency of the coco peat resulting from increasing the initial concentration of Cu(II) solution maybe due to the presence of more ions competing for the binding sites present on the coco peat's surface area.

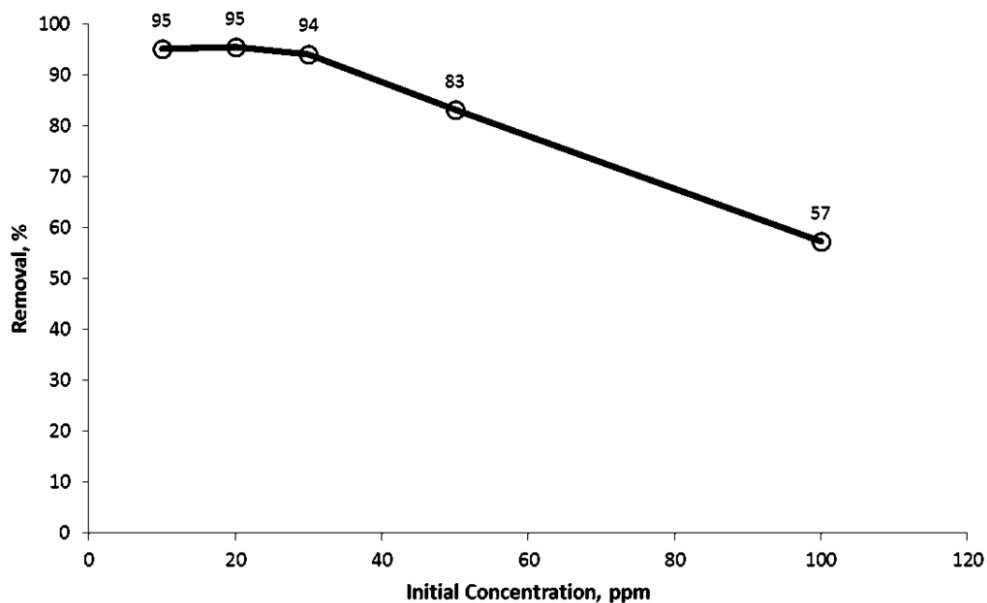


Figure 4. Cu(II) Percent removal at varying concentration

## Kinetic Studies

Adsorption kinetics explains the ability of the adsorbate to diffuse into the sorbent interior, which determines the overall adsorption rate. It is necessary to study the biosorption kinetics in order to investigate the mechanisms involved and to fully understand the sorption process. Two kinetic models were considered in the study: the pseudo-first order and the pseudo-second order models. The data obtained from the experiment varying the contact time from 5 minutes to 200 minutes were plotted using linearized forms of pseudo-first order by Lagergren and pseudo-second order models.

In 1898, Lagergren showed that the rate of adsorption of solutes on an adsorbent depends on adsorption capacity and followed a pseudo-first order equation [12]. The pseudo-first order model is expressed in the form:

$$\log (q_e - q) = \log q_e - \frac{K_{ad} t}{2.303} \quad (1)$$

where  $q$  is the amount of Cu(II) adsorbed per gram of coco peat at time  $t$  and  $q_e$  is the amount of Cu(II) adsorbed at equilibrium time in mg/g;  $t$  is the Cu(II)-coco peat contact time in minutes; and  $K_{ad}$  is the adsorption rate constant in minutes.

In 1995, Ho [12] developed a kinetic expression for the adsorption of divalent metal ions on moss peat. It was assumed that the cation-exchange capacity of the moss peat was due to the chemical bonding among divalent metal ions and the polar functional groups of the peat, such as aldehydes, acids, and phenolics. The interaction between the metal ions and the adsorbent sites leads to the assumption that the adsorption process may be second-order and that the rate-limiting step may be chemical adsorption (chemisorption) involving

the valence forces through the sharing or exchange of electrons between adsorbent and the pollutants [13]. The pseudo-second order model is expressed in the linearized form:

$$\frac{t}{q} = \frac{t}{K_{ad} q_e^2} + \left(\frac{1}{q_e}\right) t \quad (2)$$

The constant rates and correlation coefficients were derived from the graphs of  $\log(q_e - q)$  versus  $t$  and  $t/q$  versus  $t$ , as presented in Figures 5 and 6, respectively. Table 1 gives the summary of the result of the kinetic studies for pH 2.4 and 4.0.

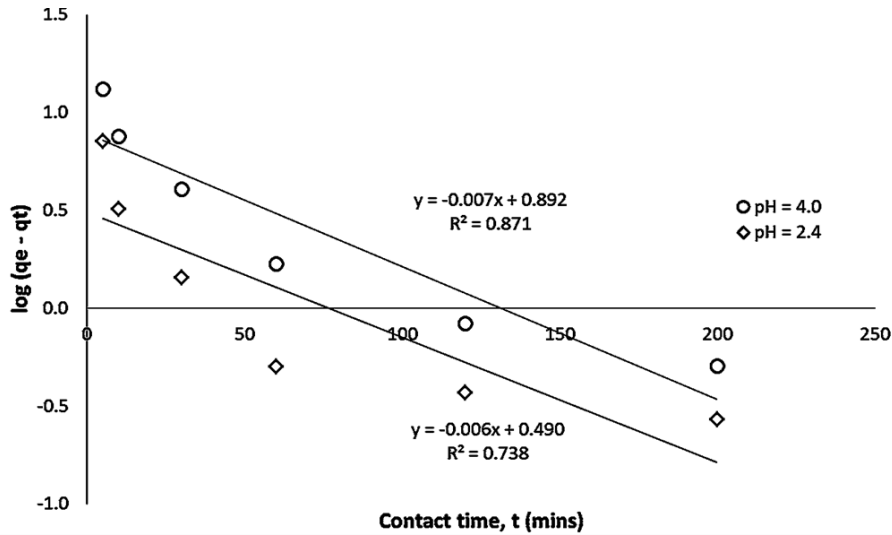


Figure 5. Pseudo-first order model for Cu(II) sorption at pH 2.4 and 4.0

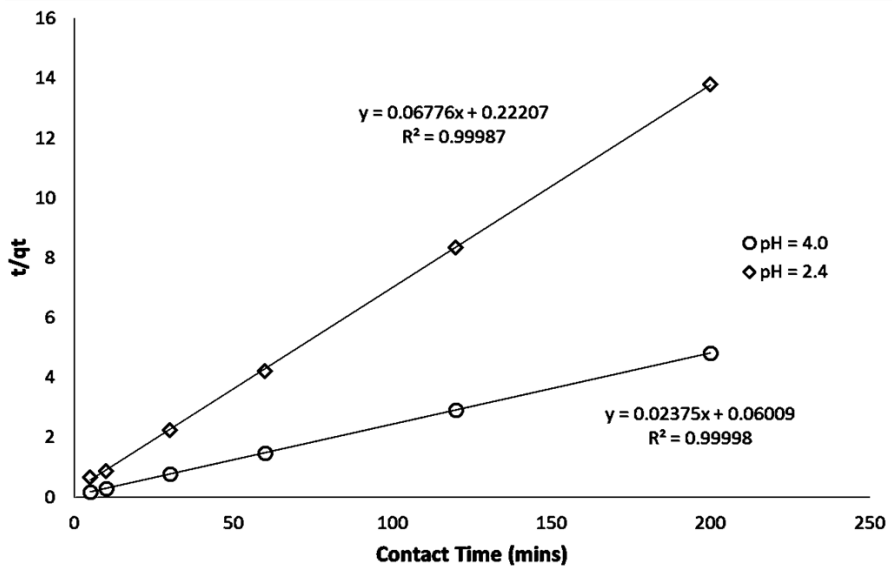


Figure 6. Pseudo-second order model for Cu(II) sorption at pH 2.4 and 4.0

**Table 1. Parameter Values for Pseudo-Second Order Model for pH4.0 and pH 2.4**

pH	4.0	2.4
qe, theo mg/g	41.6	14.5
qe, expt mg/g	41.6	14.5
$K_{ad} \text{ min}^{-1}$	0.00939	0.0207
$R^2$	0.99987	0.99998

The values of the coefficient of determination for the pseudo-second order model for pH 2.4 and 4.0 are close to unity, much higher than those obtained for the pseudo-first order kinetics. Figure 6 clearly shows that the pseudo-second order kinetic model best describes the sorption process. This verifies that chemisorption is the governing rate-limiting mechanism of the sorption process through sharing or exchange of electron between the coco peat and Cu(II) ions [8]. This result is similar with the results of the kinetic studies of sorption of lead, cadmium and copper on raw coco peat as studied by Tanchuling [4].

### Isotherm Studies

Adsorption equilibrium is also considered as important information in understanding adsorption processes [1]. The data from the batch experiment were fitted to the linearized equations of the Langmuir (Figure 7) and Freundlich isotherm (Figure 8) models. The Langmuir isotherm explains the mechanism of monolayer surface adsorption on ideal surfaces, or those with finite number of identical sites [1]. In linear form, it is given by the equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

where  $C_e$  is the equilibrium Cu(II) solution concentration in mg/L (ppm);  $q_e$  is the amount of Cu(II) sorbed at equilibrium (mg/g),  $K_L$  (L/mg) is the Langmuir constant; and  $q_m$  is the maximum sorption capacity of the Cu(II)-coco peat system.

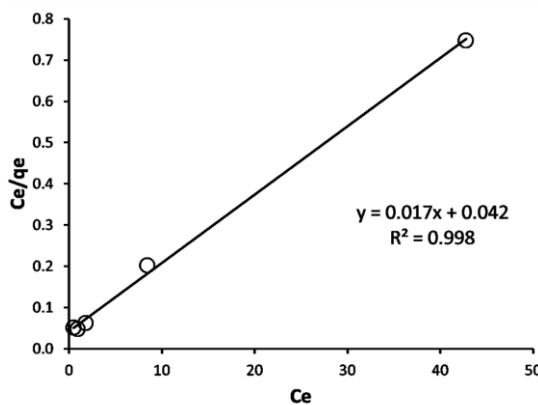


Figure 7. Langmuir isotherm plot

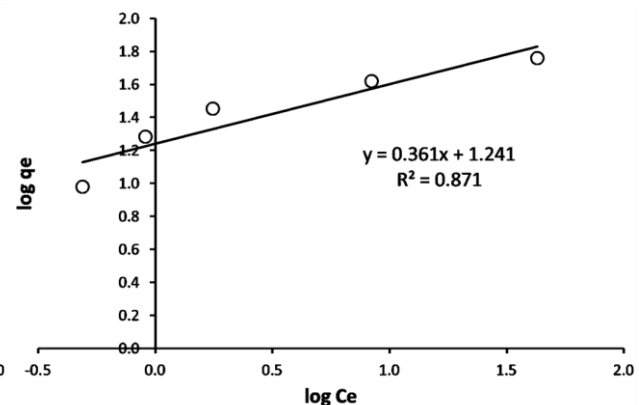


Figure 8. Freundlich isotherm plot for Cu(II) sorption

The Freundlich equation is the model used for adsorption process on heterogeneous surfaces is given by the equation:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

where,  $K_f$  is the Freundlich constant representing the sorption capacity; and  $n$  is the Freundlich constant which indicates the sorption intensity

As summarized in Figures 7 and 8 and Table 2, it can be seen that the coefficient of determination for the Langmuir isotherm model ( $R^2 = 0.99831$ ) is very close to 1.0 and is greater than the  $R^2$  value for the Freundlich isotherm model. As such, the Langmuir isotherm model is more appropriate in describing the adsorption process. This suggests that



copper ions are adsorbed onto the surface of coco peat in a homogenous and monolayer pattern.

**Table 2. Langmuir and Freundlich Isotherm Parameters for the Adsorption of Cu(II) by NaOH Pretreated Coco Peat**

Freundlich			Langmuir		
$K_f$	$n$	$R^2$	$Q_m, \text{mg/g}$	$K_L$	$R^2$
0.0936	2.77	0.871	60.2	0.394	0.998

### Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectrum of the raw and NaOH pretreated coco peat is presented in Figure 9. It can be observed that pretreatment of the coco peat with NaOH made the peak at around  $1265.30 \text{ cm}^{-1}$  disappear, indicating that NaOH pretreatment has an effect on the phenolic groups of coco peat. However, the main functional groups found in the raw coco peat remained practically unchanged after the pre-treatment.

Three samples of 0.5M NaOH pretreated coco peat were examined under the FTIR spectrophotometer: uncontaminated coco peat (clean), copper-contaminated coco peat at pH 2.4, and copper-contaminated coco peat at pH 4. Both copper-contaminated samples were contaminated at the following conditions: 0.1g dosage, 50ppm initial concentration, and 200 minutes contact time.

Comparison between the FTIR analysis of the pretreated coco peat before and after batch sorption provides insight on the involvement of certain functional groups in the sorption of Cu(II) ions. Observed changes in peak intensity in the spectrum can be indicators of sorption of Cu(II) onto the sorbent material. There is very little difference between the horizontal locations of peaks of the three samples, as illustrated in Figure 10. For simplicity, only the peaks of the uncontaminated sample will be discussed. The strong peak at  $3340.71 \text{ cm}^{-1}$  can be due to the presence of O-H stretch of hydroxyl groups, while the peak at  $2939.52 \text{ cm}^{-1}$  can be caused by the C-H stretching of alkyls [9]. The C=C stretching at  $1600.92 \text{ cm}^{-1}$  can be related with the presence of carboxyl groups. A peak at  $1512.19 \text{ cm}^{-1}$  may signify the presence of C=C bonds of lignin esters, while a peak at  $1269.16 \text{ cm}^{-1}$  may be an indicative of the presence of O-H bonds of phenolic groups. Finally, a peak at  $1033.85 \text{ cm}^{-1}$  can be associated with the presence of C-O bonds of alcohols [10].

It can be concluded that the main functional groups involved in the adsorption of copper ions to NaOH pretreated coco peat are the hydroxyl, phenolic, and carboxyl functional groups. The presence of carboxyl and hydroxyl groups showed potential as proton donors to be used in coordination with cations, which provide a possibility for coco peat to be used as a biosorbent to adsorb heavy metals. Similar observations were noted from the batch experiments on raw and sorbed coco peat by Tanchuling [4] and the study of Yazici on the effect of chemical pretreatment on Cu(II) sorption [7].

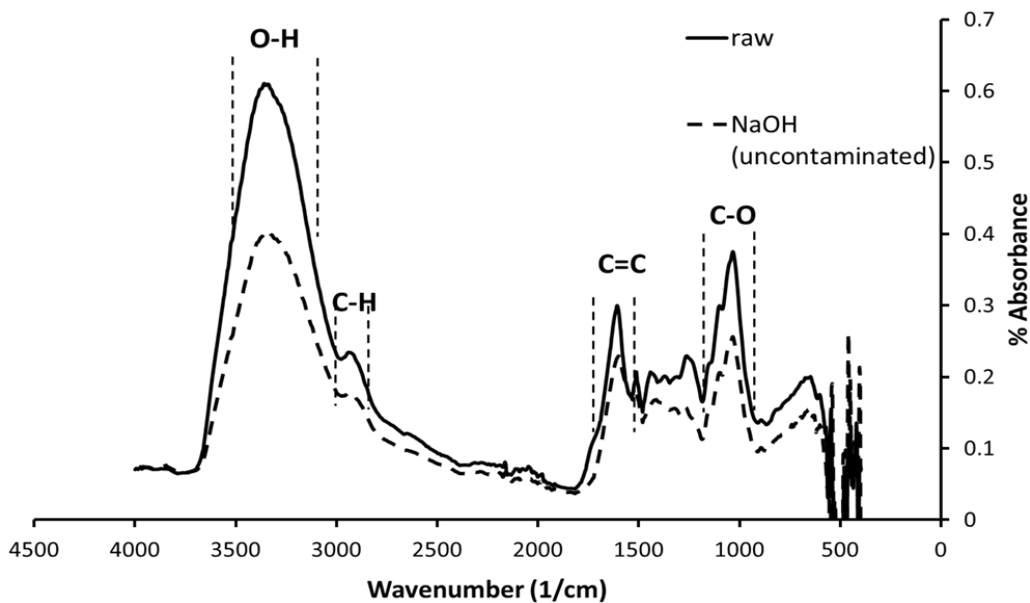


Figure 9. FTIR Spectrum of NaOH pretreated and raw coco peat

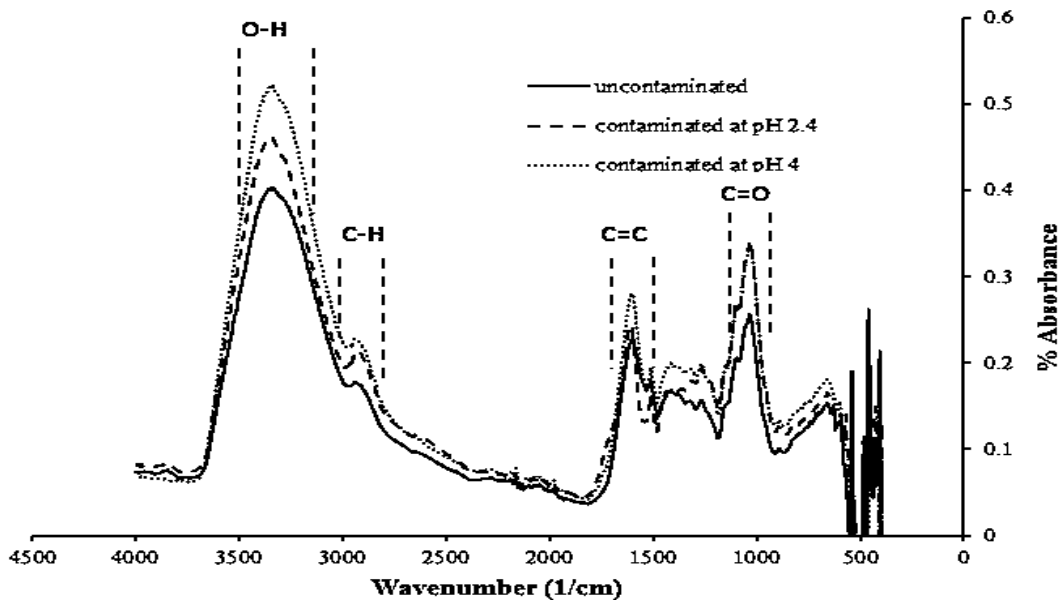


Figure 10. FTIR Spectrum of NaOH pretreated coco peat

## Conclusions

This paper studies the effect of chemically pretreating raw coco peat with NaOH on its Cu(II) sorption capacity. Based on the results of the study, it was found out that NaOH pretreatment could increase the removal capacity of raw coco peat from 46% to 83% at pH 4.0. The batch experiments showed that the removal rate is directly proportional to coco peat's dosage, solution's initial pH, and contact time and inversely proportional to the initial Cu(II) concentration. The biosorption process followed a pseudo-second order model with correlation coefficient close to unity suggesting that chemisorption is the rate-limiting step in the adsorption of Cu(II) ions to the coco peat. Langmuir isotherm better represents the sorption process rather than Freundlich isotherm indicating that the coco peat's surface is homogeneous and monolayer sorption governs. The main functional groups involved in the adsorption process are the carboxyl, phenolic and hydroxyl groups.

The highly efficient and rapid Cu(II) uptake of NaOH pretreated coco peat indicates that it could be a good alternative to conventional technologies for removal of copper from wastewater.

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