

# Sequestration of Toxic Pb (II) Ions By Base Treated Coconut (*Cocos Nucifera*) Palm Frond Powder

Mardhiah Ismail  
Megat Ahmad Kamal Megat Hanafiah  
Sarah Laila Mohd.Jan

## ABSTRACT

*The adsorption of Pb(II) ions from aqueous solution using sodium hydroxide treated coconut palm (cocos nucifera) frond powder was performed using batch experiment. The experiments were conducted to determine the factor effecting adsorption such as pH, initial heavy metal concentration and contact time. Adsorption was fast as equilibrium was achieved in less than 90 min, and was best described by pseudo-second order model. Based on the Langmuir model, the maximum adsorption capacities of Pb(II) ion was found to be 45.45 mg g<sup>-1</sup>. The highest amount of heavy metal adsorbed occurred at pH 4.*

**Kata Kunci:** *Adsorption, heavy metal*

## Introduction

The release of heavy metal into the environment creates a serious pollution problem that has become a focus of global attention. Heavy metals released to the water body create a serious health problem to organisms and reduce the quality of clean water. Heavy metals in the environment become a serious problem because of their toxicity; bioaccumulation and can spread throughout the ecosystem and threaten bio-organism. Heavy metals are not biodegradable; it will accumulate in living tissue and caused various disease and disorder (Hanafiah et al. 2010).

Lead is one of the most toxic heavy metal to organism due to the harmful effects on human biological systems such as nervous system, blood circulation, reproduction system and kidneys. Lead will also cause osteoporosis, seizures, mental retardation, memory problem and mood changes (Hanafiah and Abdulah, 2005). Normally, it originates from industrial sources such as mining process, battery manufacturing, paper and pulp processing, paint production and metal plating (Tunali et al., 2006; Li et al., 2009). This poisonous ion will get into the human body through drinking water, food and air (Bhattacharjee et al, 2003). Lead accumulates in blood, bone, muscles and fat. According to Malaysian standard, the amount of lead discharged in wastewater must not exceeded 0.10 mg L<sup>-1</sup> (standard A) and 0.50 mg L<sup>-1</sup>. Adsorption is the best choice to treat and properly remove the lead from industrial wastewater before it reaches water body.

The use of bio-adsorption technique in heavy metal removal from the environment, especially from water body is a simple and very low-cost technique because it uses an upgraded waste material. Bio-adsorption normally uses natural and agricultural waste as adsorbent. Natural materials are available in large quantity, in fact, some of the waste product from industry or agricultural have the potential to be very cheap adsorbent. Among the natural sources have been used as adsorbent includes rubber woods (Hanafiah et al. 2005), sugarcane bagasse (Osvaldo et al., 2009) olive stone waste (Nuria et al., 2005) and sea nodule (Bhattacharjee et al. 2003). The use of this technique has the advantages of helping in reducing the amount of solid waste generated from agricultural and industrial field. It is also cheap, sludge free and simple. This technique is slowly replacing the conventional method such as chemical precipitation, filtration, chemical oxidation, electrochemical treatment, ion-exchange and membrane separation.

Even though treatment of heavy metal using precipitation and filtration is cheap, but the treatment procedure is very complicated. Although the use of membrane filtration and ion-exchange is simple, the membrane and ion-exchange resins are expensive. Furthermore, most conventional methods removing heavy metals from the environment involve high energy. In addition, the use of conventional techniques is not economically practical for small and medium industry.

Modification of natural resources can enhance the adsorption capacity and recyclability of adsorbent. Modification can be performed by means of esterification, halogenations, oxidation, sulphonation etc. Even though it might also cause reducing adsorption capacity in some cases, but choosing the most suitable modification method can give optimum result. The removal of metal ion can happen through a few mechanisms including physical adsorption, chemical adsorption, precipitation, ion-exchange and etc.



The chosen of coconut palm frond is very practical since it is very cheap and highly plentiful. Coconut palms are grown in more than 80 countries of the world, with a total production of 61 million tons per year. In Malaysia, coconut palm fronds are commonly left to decompose or be burned which could diminish the air quality. Besides, it has various functional groups such as hydroxyl, carbonyl, phosphate and etc that can chelate or bind with metal ion.

## Objectives

Generally, the main objectives of this study were to prepare and to understand the mechanism of lead ions removal onto base treated *cocus nucifera* frond powder. The effect of certain important physiochemical parameter which can affect lead adsorption such as pH, contact time and initial lead concentration were discussed. Determination of rate determining step was performed by applying two kinetic models (pseudo-first order and pseudo-second order). The mechanisms of adsorption were determined using spectroscopic and quantitative analyses.

## Experimental

### Adsorbent preparation

Dried coconut palm frond was collected from a residential area at Sungai Isap Damai, Kuantan. The palm frond was washed several times with distilled water to remove dust and soluble impurities and was dried in the oven overnight at 80°C. The dried palm frond was grinded using mechanical grinder and sieved to get a geometrical size ranging from 125-355  $\mu$ m.

30 g of the dried palm frond powder was mixed with 0.05 M NaOH solution and stirred at 500 rpm for 2 hours. The adsorbent then was filtered and washed several times with distilled water until the pH of the desiccant became constant at 9.80. The treated palm frond powder was dried in the oven at 80°C overnight. The dried treated palm frond powder was then kept in the airtight container for further uses.

### Preparation of lead solution

Analytical grade 1000 mg/L lead nitrate ( $\text{PbNO}_3$ ) solution (Merck) was diluted with de-ionized distilled water to get the concentration of 5 mg/L and 10 mg/L. Fresh dilution was prepared for each experiment.

### Adsorption study

Batch adsorption experiments were carried out in a series of 100 mL conical flask. 0.100 g adsorbent (unless otherwise stated) was placed into a conical flask that was initially added with 50 mL standard solution with a desired concentration. The flask was shaken in the water bath shaker at 120 rpm.

The amount of lead ion adsorbed ( $q$ ) in the adsorption system was calculated using the following equation:

$$q = \frac{(C_i - C_f)}{m} \cdot V \quad q = \frac{(C_i - C_f)}{m} \cdot V$$

Where  $C_i$  and  $C_f$  are the initial and equilibrium lead concentration,  $V$  is the volume of lead solution and  $m$  is mass of the adsorbent. Meanwhile, the percentage of lead removal from aqueous solution is calculated using the following equation:

$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad \% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \times 100$$

### Effect of initial lead concentration and contact time

To study the initial lead concentration effect on the removal efficiency, the synthetic lead solution with the concentration of 10 and 5 mg/L were prepared. The mass of the adsorbent use for this study was 0.100 g and the agitation time was varied for 0, 1, 3, 5, 7, 10, 15, 20, 30, 60 and 90 minutes at 31°C. The flask was withdrawn from the shaker at a predetermined time and the reaction mixture was filtered through Whatman filter paper.

### Effect of pH on lead removal

The effect of pH on the removal of lead from solution was analyzed between pH 1.0 to 4.0. The experiment was performed using 0.100 g adsorbent which was added into 50 mL of lead solution. The conical flask was agitated at 120 rpm, 31°C for 90 min. The initial pH was adjusted using 0.1 M NaOH and 0.1 M HNO<sub>3</sub>. The pH was measured using a glass electrode.

### Isotherm plot

A lead solution with concentration of 5, 10, 15, 20, 25, 30, 50, 75 and 100 mg/L were prepared in a series of conical flask. The pH of each solution was adjusted to 4.0. Then, 0.100 g adsorbents were added into each flask and were shaken at 120 rpm for 90 min at 31°C.

## Results and Discussion

### Adsorption Isotherm

Adsorption isotherm shows the relationship between amount of adsorbate adsorbed per unit weight of adsorbent ( $q_e$ , mg g<sup>-1</sup>) and the concentration of adsorbate in bulk solution ( $C_e$ , mg L<sup>-1</sup>) at a given temperature and under equilibrium condition. Adsorption equilibrium is achieved when the amount of adsorbate being adsorbed was equal to that being desorbed. At this stage, the equilibrium concentrations in both phases were constant. Adsorption isotherm is very useful in explaining adsorption mechanism, providing information about surface properties and affinity of an adsorbent toward metal ions (Porter & Mc Kay et al., 2002).

The experimental isotherm data for this experiment is shown in Fig 1. The plot shows that the adsorption capacities of the adsorbent increase with the increasing lead initial concentration.

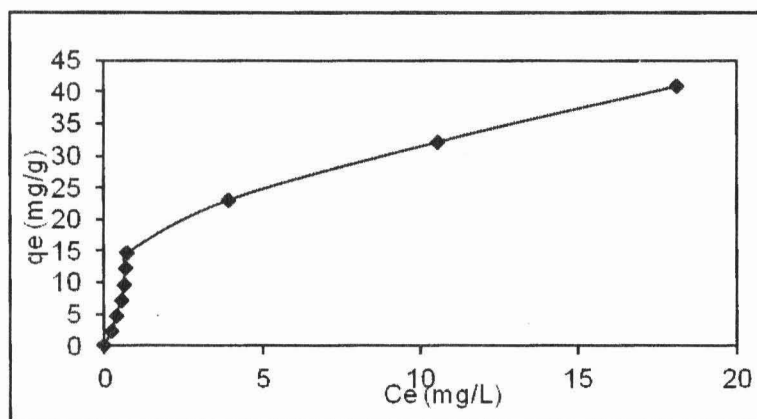


Figure 1: Adsorption isotherm plot of lead

At low concentration there is a sharp increase in adsorption capacity, as concentration increased to more than 50 mg L<sup>-1</sup>, the increment in adsorption capacity is low. This means that at low concentration, the adsorbent had sufficient number of adsorption site to uptake lead ion. At higher concentration, the ratio of heavy metal ion to adsorption sites increased. As a result, the un-adsorbed lead ions remain in bulk solution.

### Langmuir isotherm

Langmuir isotherm is the most widely applied isotherm model in adsorption study. The model assumes that adsorption occurs at specific homogeneous site on the adsorbent (Langmuir, 1916). This model was successfully used in monolayer adsorption process.

The Langmuir plot for this analysis is shown in Fig. 2. The summary of Langmuir constant (b), maximum adsorption capacity and correlation coefficient are tabulated in table 1.

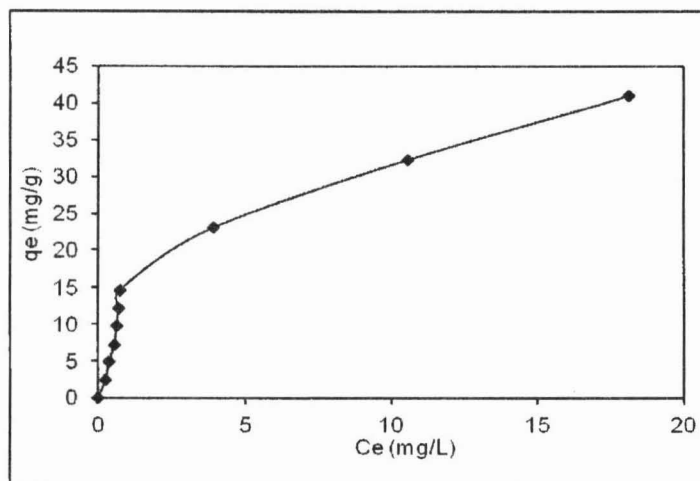


Figure 2: Langmuir isotherm plot of lead

Table 1: Langmuir constant and correlation coefficient for lead.

Langmuir		
$q_{\max}$ (mg g <sup>-1</sup> ),	B (L mg <sup>-1</sup> )	R <sup>2</sup>
45.45	0.344	0.9719

The Langmuir plot is linear with the value of correlation coefficient very close to 1 indicating that the adsorption of lead ion onto adsorbent followed the Langmuir model. The maximum adsorption capacity of the adsorbent calculated from the model is 45.45 (mg g<sup>-1</sup>) and close to the experimental value, 40.94 (mg g<sup>-1</sup>).

### Freundlich isotherm

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer or heterogeneous adsorption surface. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The strongest adsorption will be occupied rapidly and the strength of binding decreased with the increasing the degree of site being occupied.

The Freundlich equation is given by (Freundlich, 1906):

$$q_e = K_f C_e^{1/n} \quad (\text{non-linear form})$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (\text{linear form})$$

Where  $K_f$  is Freundlich constant that is related to maximum adsorption capacity (mg g<sup>-1</sup>) and  $n$  is related to adsorption intensities which is unitless. If the value of  $n$  is greater than 1, it shows that the adsorption is favorable. The higher the  $n$  value the stronger the adsorption intensities. The Freundlich plot for this analysis is shown in Fig.3. The summary of the maximum adsorption capacity ( $K_f$ ), the adsorption intensity value ( $n$ ) and correlation coefficient are tabulated in Table 2.

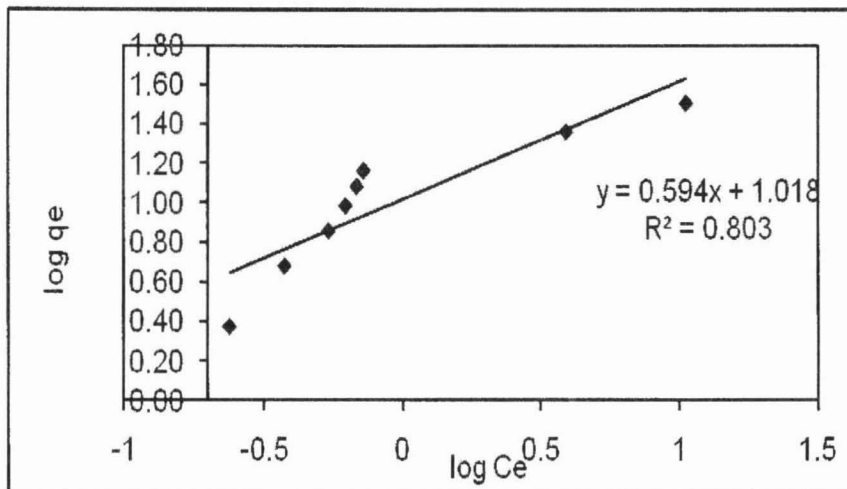


Figure 3: Freundlich isotherm plot of lead

Table 2: Freundlich constant and correlation coefficient for lead.

Freundlich		
$K_f$ (mg g <sup>-1</sup> ),	n	R <sup>2</sup>
10.435	1.68	0.8035

The Freundlich plot is linear, but the value of correlation coefficient and maximum adsorption capacity,  $K_f$  are lower than Langmuir. This indicated that the adsorption of lead ion onto adsorbent did not fit well with the Freundlich model. The n value is in between 1 to 10 the adsorption process is favorable.

### Adsorption kinetic model

Three kinetic models named as pseudo-first order, pseudo-second order and Boyd were applied to determine the adsorption rate of adsorbent. Adsorption kinetic is important in providing the information on rate determining steps. Adsorption kinetic depends on various kinds of mechanism such as film diffusion, pore diffusion or chemical reaction; complexation or ion-exchange (Ofomaja, 2008). It is a normal practice to evaluate the correlation coefficient ( $R^2$ ) of a kinetic model and to compare their adsorption capacity to confirm the agreement between experimental and model's predicted values.

### Pseudo-first order

The pseudo-first order kinetic model assumes that the adsorption rate is proportional to the number of free binding sites. The linear form of pseudo-first order is given by (Ho and McKay, 1998):

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

Where  $q_e$  and  $q_t$  are adsorption capacity (mg g<sup>-1</sup>) at equilibrium and at time t (min) and  $k_1$  is the pseudo-first order rate constant (min<sup>-1</sup>). A slope and intercept of graph of  $\log(q_e - q_t)$  versus time (t) will give the values of  $k_1$  and  $q_e$  respectively. The pseudo first order graph for lead adsorption at 5 and 10 mg L<sup>-1</sup> is shown in Fig. 4 and 5 respectively.

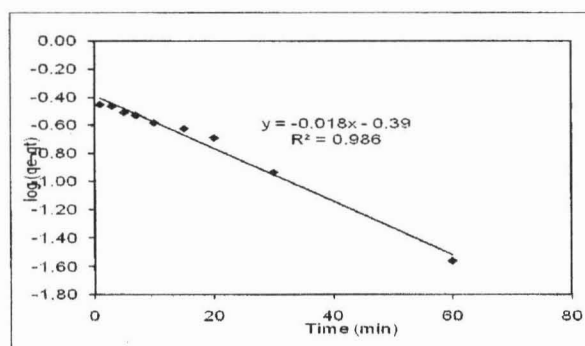


Figure 4: Pseudo-first order plots of lead adsorption at 5mg L<sup>-1</sup>

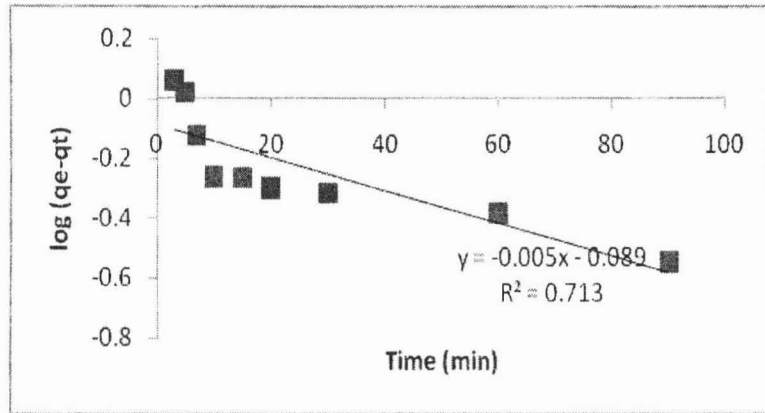


Figure 5: Pseudo-first order plots of lead adsorption at 10 mg L<sup>-1</sup>

This kinetic model is followed if the graph show good linearity ( $R^2 > 0.95$ ) and the calculated adsorption capacity ( $q_{e,cal}$ ) in agreement with experimental adsorption capacity ( $q_{e,exp}$ ).

Table 3: The pseudo-first order constant and correlation coefficient for lead.

Pb Conc. (mg L <sup>-1</sup> )	$q_{e, exp.}$ (mg g <sup>-1</sup> )	Pseudo-first order		
		$q_{e, cal.}$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$
5	2.3805	0.958	0.898	0.9868
10	2.216	0.987	0.206	0.713

All the equilibrium capacity, rate constant and correlation coefficient of pseudo-first order for this study are shown in Table 3. In general, both plots showed linearity. The value of relation coefficients for 5 mg L<sup>-1</sup> is almost unity (0.9868) but for 10 mg L<sup>-1</sup> is very far from unity (0.713). However, the calculated adsorption capacity ( $q_{e,cal}$ ) for both concentration were not in agreement with experimental adsorption capacity ( $q_{e,exp}$ ).

In general, the rate is constantly decreased with the increasing of lead concentration. At low concentration of lead (5 mg L<sup>-1</sup>) the rate constant is 0.898 min<sup>-1</sup>, as the concentration increased (10 mg L<sup>-1</sup>) the rate constant reduced to 0.206 min<sup>-1</sup>. This shows slower uptake of lead ions as concentration increase because the competition for adsorption site at higher concentration is also high. From the pseudo-first order model suggest that boundary layer resistance might not be the major rate determining step in this system.

### Pseudo-second order

Pseudo-second order is based on the assumption that the rate determining step of the adsorption process is chemisorptions. The equation is expressed as (Ho and McKay, 2000):

$$\frac{t}{q} = \frac{1}{h} + \frac{1}{q} t$$

Where  $h = k_2 q_e^2$ , when  $t \rightarrow 0$ ,  $h$  can be considered as the initial adsorption rate (mg g<sup>-1</sup> min<sup>-1</sup>) for pseudo-second order adsorption. The plot  $t/q$  versus  $t$  will give a straight line if pseudo-second order is applicable for the system. The value of  $k_2$  and  $h$  can be obtained from the slope and intercept respectively.

The pseudo-second order graph for lead adsorption at 5 and 10 mg L<sup>-1</sup> are shown in Fig. 6 and 7 respectively. The linearity of the plot is better with the  $R_2$  are very close to 1 compare to pseudo-first order. Furthermore, the value of the calculated adsorption capacity ( $q_{e,cal}$ ) were almost similar to the experimental adsorption capacity ( $q_{e,exp}$ ) as shown in table 4. From this finding, one can conclude that the rate determining step for this system was likely due to the chemisorptions which involve sharing or exchanging the electrons between the adsorbate and adsorbent (Ho and McKay, 1998). The rate constant for pseudo-second order ( $K_2$ ) also decreased as concentration increased. This can be explained by competition for adsorption site between lead ions.

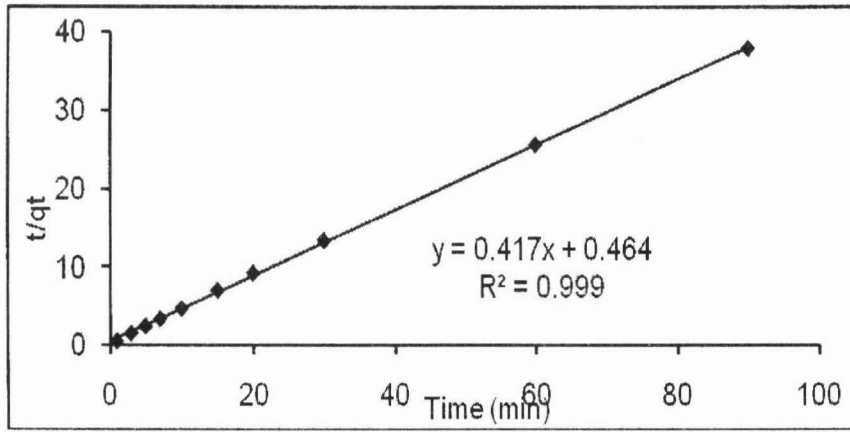


Figure 6: Pseudo-second order plots of lead adsorption at 5 mg L<sup>-1</sup>

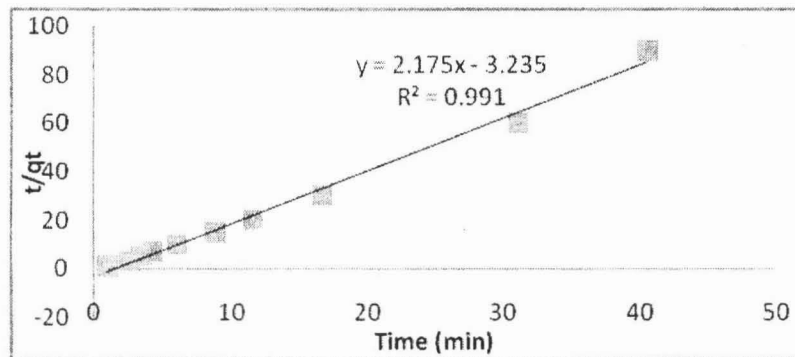


Figure 7: Pseudo-second order plots of lead adsorption at 10 mg L<sup>-1</sup>

Table 4: The pseudo-second order constant and correlation coefficient for lead

Pb Conc. (mg L <sup>-1</sup> )	qe, exp. (mg g <sup>-1</sup> )	Pseudo-second order		
		qe, cal. (mg g <sup>-1</sup> )	K <sub>2</sub> (min <sup>-1</sup> )	R <sup>2</sup>
5	2.3805	2.397	0.375	0.9996
10	2.216	0.4596	1.469	0.9918

## Conclusion

Based on this experiment, the adsorption of lead ion by base treated (*cocos nucifera*) palm frond occurred in less than 90 min. The adsorption of lead was found to best fit with Langmuir isotherm model which give the maximum adsorption capacity of 45.45 (mg g<sup>-1</sup>). Lead adsorption is pH dependent and the optimum pH for this study is 5. Initial lead concentration had a significance influence on the kinetic of the adsorption process. Pseudo-second order kinetic model was fitted for the adsorption of Pb (II) ions onto adsorbent.



## References

- Freundlich, H. (1906). Over the adsorption in solution. *Z.Phys.Chem.*, 57, 385-470. Retrieved from [www.scopus.com](http://www.scopus.com)
- Ho, Y. S., and McKay, G. (1998). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environmental Protection*, 76(4), 332-340. Retrieved from [www.scopus.com](http://www.scopus.com)
- Ho, Y. S., and McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Research*, 34(3), 735-742. Retrieved from [www.scopus.com](http://www.scopus.com)
- Ho, Y. S., Porter, J. F., and McKay, G. (2002). Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. *Water, Air, and Soil Pollution*, 141(1-4), 1-33. Retrieved from [www.scopus.com](http://www.scopus.com)
- Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. part I. solids. *The Journal of the American Chemical Society*, 38(2), 2221-2295. Retrieved from [www.scopus.com](http://www.scopus.com)
- Ofomaja, A. E. (2008). Sorptive removal of methylene blue from aqueous solution using palm kernel fibre: Effect of fibre dose. *Biochemical Engineering Journal*, 40(1), 8-18. Retrieved from [www.scopus.com](http://www.scopus.com)