



SEPARATION OF Pb(II) FROM WASTEWATER USING UNTREATED COCONUT (*Cocos nucifera*) FROND POWDER

(Pengasingan Pb(II) daripada Air Buangan Menggunakan Serbuk Pelepah Kelapa (*Cocos nucifera*) yang Tidak Dirawat)

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Abstract

The adsorption of Pb(II) ion from wastewater by coconut frond powder was evaluated in the batch adsorption process. Characteristic of the coconut frond powder (CFP) was determined by performing a pH_{zpc} analysis and also infra-red spectroscopy analysis for the investigation of the functional group on CFP surface. The batch adsorption study was carried out using five parameters including the effect of pH, the effect of adsorbent dosage, the effect of initial concentration and contact time, the kinetic and isotherm study. The optimum dosage used in this study was 0.04 g while the optimum pH for the adsorption of lead ions was pH 4. The adsorption capacities depended on lead concentration and contact time. It required a relatively short period of time to reach an equilibrium which is less than 60 minutes. Two kinetics models; pseudo first order and pseudo second order were used to analyze the lead adsorption process. Pseudo second order model was found to fit well enough the experimental data compared to pseudo first order.

Keywords: adsorption, *Cocos nucifera*, kinetic, lead

Abstrak

Penjerapan Pb(II) ion daripada sisa air oleh serbuk pelepah kelapa telah dinilai menggunakan proses penjerapan secara berkelompok. Ciri-ciri serbuk pelepah kelapa (CFP) telah ditentukan dengan menjalankan analisa pH_{zpc} dan juga spektroskopi infra-merah untuk mengkaji kumpulan-kumpulan berfungsi pada permukaan CFP. Kajian penjerapan berkelompok telah dijalankan dengan menilai lima parameter termasuk kesan pH, kesan dos penjerap, kesan kepekatan awal dan masa penjerapan, kajian kinetik dan kajian isoterma. Dos penjerap yang optimum diperolehi adalah 0.04 g sementara pH optima adalah pH 4. Kapasiti penjerapan bergantung kepada kepekatan larutan plumbum dan masa tindak balas. Proses penjerapan memerlukan masa yang pendek untuk mencapai keseimbangan iaitu kurang daripada 60 minit. Dua model kinetik; pseudo peringkat pertama dan pseudo peringkat kedua telah digunakan untuk menilai proses penjerapan plumbum. Model pseudo peringkat kedua didapati lebih sesuai untuk membincangkan data kinetik berbanding model pseudo peringkat pertama.

Kata kunci: penjerapan, *Cocos nucifera*, kinetik, plumbum

Introduction

The presence of heavy metal in the aquatic environment has become a great concern to scientist and also world community due to the toxic nature and negative effect on the receiving water. The major sources of the heavy metal come from industries such as metal electroplating, mining, painting, plumbing, battery manufacturing and many other industries [1,2].

The word heavy metal attribute to any metallic element that has a relatively high density, specific gravity or atomic weight. The heavy metal is toxic and poisonous even at low concentration. Heavy metals exist naturally in the Earth's crust and also being released into surrounding due to human activities. It can be found in water, sediment, soil, microorganism and rock with natural background concentration. Heavy metals cannot be degraded and destroyed; hence, it will persist in the environment [3]. An example of heavy metals includes mercury, lead, cadmium, arsenic, copper, iron, and thallium. When absorbed by human body, it can cause the physiological and neurological disorder. Heavy metal can enter human bodies via food, air, and drinking. Some heavy metals such as copper, selenium, and zinc are fundamental to maintain the metabolism of the human body. However, at higher concentration, heavy metal can lead to poisoning through high ambient air concentration near emission sources or via the food chain.

Lead can be considered as a hazardous metal due to its negative effect on the human nervous system, blood circulation system, kidneys and reproductive system[4,5]. Usually, the common victim of lead poisoning is children and it can cause mental retardation and semi-permanent brain damage. Due to its toxicity and carcinogenic properties, it causes a serious threat to the human population and also flora and fauna when the lead discharged into wastewater. Lead get into the human body via inhalation, ingestion, and skin adsorption. It can affect organ and system in human body. It is necessary to discard this toxic heavy metal from wastewater before it is disposed of as this will avoid and reduce health hazard to both mankind and another living organism. Hence, lead from industrial wastewater must be properly treated to avoid it from reaching the water bodies. There are a few physicochemical methods that have been introduced in the removing of heavy metals from wastewater such as chemical precipitation, chemical coagulation, ultrafiltration, using natural zeolite ion exchange, adsorption, and electrochemical deposition. Many researchers have focused on untreated plant waste such as papaya wood [6], garlic peel [7], cotton [8, 9]. There are many advantages of using plant waste as an adsorbent in the treatment of wastewater such as it is a simple technique, low operation cost, great adsorption capacity, can be regenerate and the ability to adsorb heavy metal ions. However, besides the advantages of untreated plant waste, they also bring some problems such as low adsorption capacity, high in chemical oxygen demand (COD), biological chemical demand (BOD), and total organic carbon (TOC). This happened due to the release of the soluble organic compound in the plant materials [10, 11]. Plant material can be divided into a few parts such as fruit, flower, bark, leaf and others. All part of the plant has been studied as an adsorbent.

A coconut tree, known as (*Cocos nucifera*) is a member of the *Areaceae* (palm family). It is also known as “the tree of life” since it gives many benefits to the human and living organisms such as sources of food and medicine. Normally, *Cocos nucifera* grows up to 30 meters tall. It has pinnate leaves with 4-6 meter long, and pinnae 60-90 cm long [12]. The leaves will break away when it old and leave the trunk smooth. The coconut is very nutritious and highly in fiber, vitamins, and minerals. The coconut oil is used in traditional medicine among Asian and pacific population since it contains healing properties compared to any other dietary oil. This tree consists of a few parts which are a shell, fruit, coconut frond and others. The various part of the coconut has been extensively studied as bio-sorbents for removal of pollutants from water [13]. Coconut frond was first used [14] in removing carbofuran insecticides by mesoporous activated carbon from coconut frond. The treated spent grated coconut shows high adsorption capacity compared to the untreated spent grated coconut which is 366.50 mg/g. Treatment of spent grated coconut with acid increased the adsorption capacity due to the increasing of surface area and pores. Previous research [15] were performed a research on sulphuric acid treated coconut (*Cocos nucifera*) frond powder in removing methylene blue from aqueous solution. In this study, untreated coconut frond powder will be used for removing Pb(II) from aqueous solution. Literature also has shown that untreated coconut frond in removing Pb(II) never been conducted as well.

Materials and Methods

Adsorbent preparation

Coconut frond was collected from Kelantan, Malaysia. The frond was washed to remove soluble impurities before rinsing with deionized water and was dried in an oven at 333 K to avoid any sample degradation overnight before being ground and sieved by using a mechanical grinder to obtain a particle size of 125-250 μm . The newly prepared

coconut frond powder was labeled as CFP (coconut frond powder). The CFP was used as adsorbent without any chemical treatment.

Adsorbent characterization

The determination of pH_{ZPC} of CFP was performed according to the solid addition method as reported by Balistrieri and Murray [16]. A 50 mL of 0.01 M KNO_3 solution was placed into 8 different 100 mL conical flasks. The initial pH of the solutions was adjusted to a value between pH 2-9 by adding 0.1 M HCl or NaOH solutions. Then, 1 g of CFP was added to each flask, stirred and the final pH of the solutions was measured after 24 hours. The value of pH_{ZPC} can be determined from the curve that cuts the pH line of the plot ΔpH versus initial pH. The type of functional groups presents in the CFP was determined by using a Fourier transform infrared spectrometer (FTIR) (Perkin Elmer, Spectrum 100, USA).

Adsorption experiment

Lead nitrate ($Pb(NO_3)_2$, MW = 331.2 g mol⁻¹) was purchased from MERCK, Malaysia. The stock solution of 1000 mg L⁻¹ Pb(II) was prepared and diluted to the preferred concentrations with deionized water. The effect of dosage was performed by mixing 0.02, 0.04, 0.06, 0.08 and 0.1 g CFP with 50 mL (10 mg L⁻¹) Pb(II) and stirred at 120 strokes per minute at 298±1 K for 90 min to achieved equilibrium. The effect of pH was studied in the pH range between 2 to 4. Adsorption kinetic study was conducted using three different Pb(II) concentrations (10, 20 and 30 mg L⁻¹) at various contact times (0-90 minutes). After adsorption, the CFP was filtered and the final concentration of Pb(II) was determined by using Atomic Absorption Spectrometer (PinAAcle 900T, Perkin Elmer, USA). All experiments were conducted in duplicate and the RSD values for all analyses were less than 5%. The amount of Pb(II) ion adsorbed (q_e , mg g⁻¹) and percentage removal (%) was calculated by using equations (1) and (2), respectively:

$$q_e = \frac{C_i - C_e}{m} V \quad (1)$$

$$\text{Removal}(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where C_i and C_e are the initial and final concentrations (mg L⁻¹) of Pb(II) and m is the weight of CFP (g).

Results and Discussion

Adsorbent characterization

The pH_{zpc} is important to determine the pH where the surfaces of the adsorbent exhibit zero electrical charges. It also gives important information on the electrostatic interaction between the adsorbent and the adsorbate. The pH_{zpc} for coconut frond powder (CFP) was determined at 5.45. At this point, the functional group of the adsorbent is no longer contributed to the pH of the solution. At the point where the pH is lower than pH_{zpc} value, the adsorbent surface will carry a positive charge (attract anion) while when the pH is higher than pH_{zpc} value, the adsorbent will carry negative charge ion (attract cation).

FTIR analysis was carried out in order to reveal the active functional on the surface of the CFP that might be involved in the adsorption process. The FTIR spectra of CFP before and after adsorption were shown in Fig. 1 below. The spectra display a number of adsorption peak, indicate the nature of a functional group of CFP that consist of complex functional groups such as amino, hydroxyl, and carbonyl. All these groups have possibility can have a chemical interaction with Pb(II) ion. After adsorption with Pb(II) ion, many functional groups shifted to a different wavenumber which can be a confirmation that CFP has chemical or physical interaction with Pb(II) ion. The strong and broad peak at 3331 cm⁻¹ indicates the presence of O-H stretching vibration due to the alcohol, phenols and carboxylic acid [17]. However, after the adsorption, the peak slightly shifted to a lower band of 3289 cm⁻¹. The peak that observed at 2922 cm⁻¹ can be appointed to asymmetric and symmetric -CH₂ group [18].

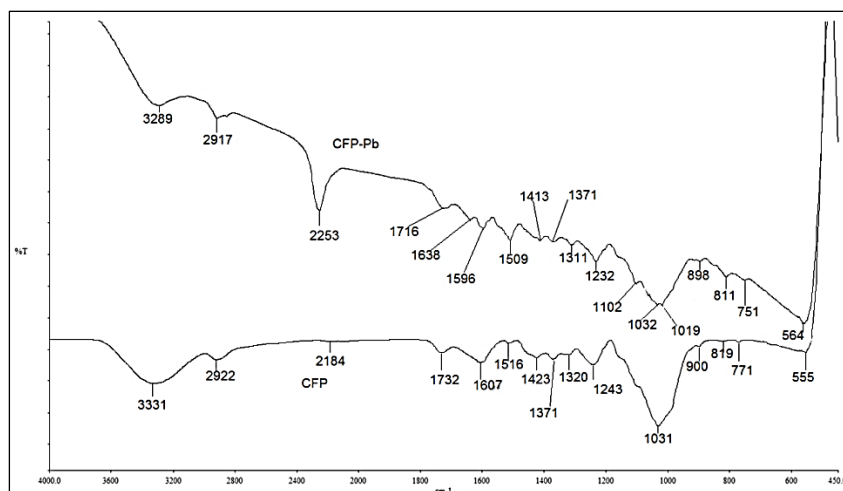


Figure 1. FTIR spectra for CFP and CFP-Pb after adsorption

The minor peak at 2184 before adsorption shifted to a higher frequency of 2253 cm^{-1} after the adsorption. The peak corresponds to the alkene group C=C. The peak at 1732 cm^{-1} before adsorption shifted to the lower band at 1716 indicate the presence of carbonyl group C=O. N-H bond for primary and secondary amines and amide appear at peak 1607 cm^{-1} before adsorption and slightly increase after adsorption to 1637.64 cm^{-1} . Besides that, the C-O group (alcohols, ether, esters, carboxylic acids, anhydrides) appeared at peak ranging from 1300-1000 cm^{-1} . The small peak observed at 1517 cm^{-1} is due to $-\text{NH}_2$ group [19], the frequency decrease after the adsorption of lead Pb(II) to 1509 cm^{-1} . Based on spectroscopy analysis, it can be concluded that the functional group responsible for the adsorption of Pb(II) onto CFP are carbonyl and amine groups which have a partial negative of oxygen and nitrogen that attracted toward a positive charged of Pb(II) ions.

Study of pH

The effect of pH on adsorption of Pb by CFP (Fig. 2) was studied in the pH ranges from 2 to 5 with an adsorbent dosage of 0.04 g and adsorbate concentration of 10 mg L^{-1} . pH 5 and above were not chosen because precipitation of $\text{Pb}(\text{OH})_2$ will occur and to ensure that only Pb(II) involved in the adsorption studies [20]. The result of the effect of pH is illustrated in Fig. 2 below. From the result, the amount of Pb(II) ion adsorbed increased with the increasing of pH value. At pH 2, the amount of Pb(II) adsorbed was the lowest amount among the others which was 1.71 mg g^{-1} . The highest adsorption of Pb(II) occurs at pH 5 (11.79 mg g^{-1}). The adsorption capacity of Pb(II) lows at pH 2 because Pb(II) ion need to compete with H_3O^+ for adsorption site. When the pH increased, the competing effect of H_3O^+ decreased and more adsorbent surface were revealed, the positive Pb(II) ions could easily adsorbed on the available adsorption sites of the adsorbents. The Pb(II) ion carried a positive charge and result in less repulsion of Pb(II) ion with the negative adsorption pH at high pH value contribute to high adsorption at higher pH (between pH 3-5). Pb(II) ion usually present at pH less than 5 and it is suitable to use in adsorption study. The pH adsorption edge in this experiment was between 2 to 4. At pH higher than 5, Pb(II) ion adsorbed will decrease due to the formation of $\text{Pb}(\text{OH})_2$. Hence, the applicable pH for adsorption of Pb(II) ion in this experiment was pH 4.

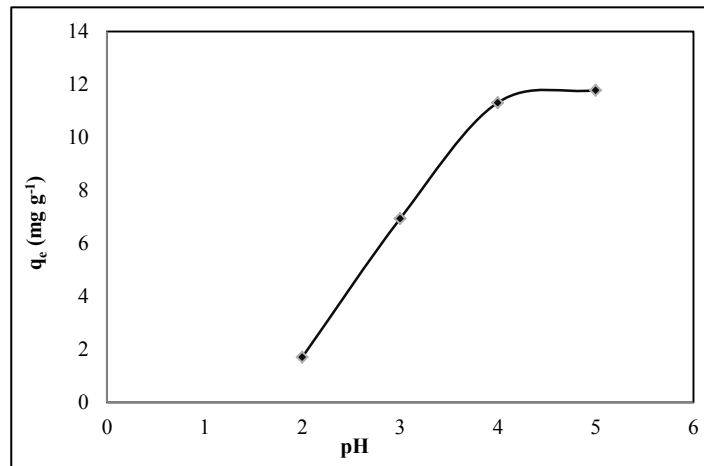


Figure 2. Effect of pH on adsorption of Pb onto CFP

Study of dosage

Fig 3 shows the removal of Pb(II) as a function of CFP dosage. Based on the result obtained, when the dosage increased from 0.02 g to 0.1 g, the percentage removal increased from 52.3 to 93.26% but inversely the adsorption capacity decreased gradually from 13.08 to 4.66 g mg⁻¹. This might happen due to the availability of more binding sites as there is more adsorbent is added with the same amount of Pb(II) [21]. The amount of Pb(II) adsorbed remains constant above 0.06 g. As the number of adsorption site increased and heavy metal concentration was fixed at a similar concentration (10 mg L⁻¹), there will be a lot of un-adsorbed adsorption sites. According to the result obtained, the adsorbent dosage of 0.04 g showed both relatively high percentage removal and high adsorption capacity. As a result, 0.04 g was used for further adsorption parameter in this study.

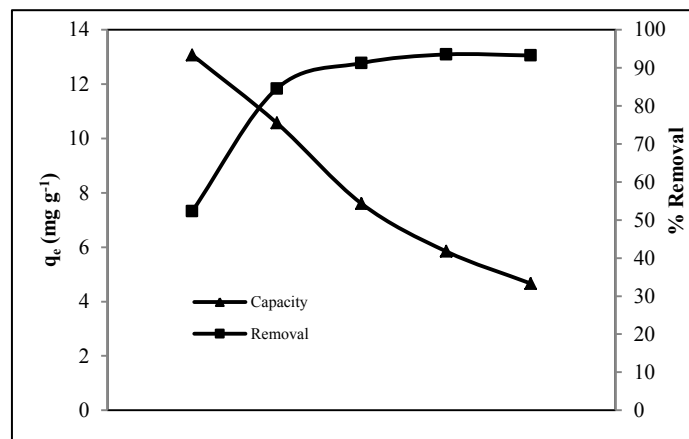


Figure 3. Effect of CFP dosage on the Pb adsorption onto CFP

Study of initial Pb(II) ion concentration and contact time

The effect of lead concentration and contact time are important factors to determine the kinetic of adsorption. The adsorption data at different initial Pb(II) concentrations and contact time are shown in Fig 4. The adsorption process was carried out at different contact times and initial concentration of Pb(II) with constant adsorbent dose (0.04 g) at room temperature. Based on the graph, the adsorption capacity and equilibrium time depended on the concentration of Pb(II). The adsorption reached equilibrium within 10 minutes for the lead concentration of 10 and 20 mg L⁻¹ and

30 minutes for 30 mg L⁻¹. The amount of Pb(II) adsorbed at equilibrium were 11.06 mg L⁻¹, 19.51 mg L⁻¹ and 34.96 mg L⁻¹ for the concentration of 10, 20 and 30 mg L⁻¹ respectively. At the initial stage, large capacity of the available bare surface area of the adsorbent was favorable for the adsorption of the Pb(II) and after an equilibrium time, the pores of the coconut frond (CFP) are fully saturated with the Pb(II) molecules and adsorption process becomes constant. This is happening because the remaining available sites of the CFP compete among the Pb(II) molecules due to the steric effect as well as repulsive forces, and as the number of empty adsorption site decrease compare with the number of lead ion available, the rate of the adsorption slowing down [22]. From the result obtain in this study, we can see that the amount of the Pb(II) molecules adsorbed per unit mass of CFP increase with an increase in the initial concentration of Pb(II) which caused by the high concentration gradient at high concentration that acts as a driving force for the adsorption process.

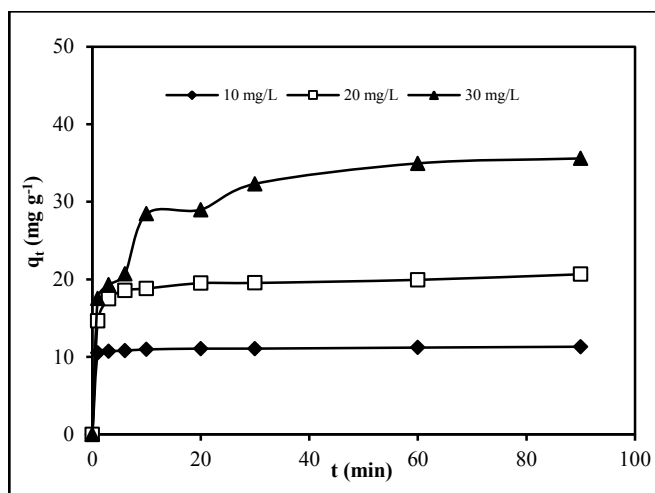


Figure 4. Effect of initial concentration and contact time on adsorption of Pb onto CFP

Adsorption kinetic model

The kinetic data for the adsorption of Pb(II) were further analyzed by using the pseudo first order and pseudo second order kinetic models. The equations for both kinetic models were expressed in equation (3) and (4) respectively:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e is the amount (mg g⁻¹) of Pb(II) adsorbed onto CFP at equilibrium and q_t is the amount (mg g⁻¹) of Pb(II) adsorbed at any time t (min) while K_1 and K_2 are the rate constants of pseudo-first-order and second-order models, respectively. While $K_2 q_e^2$ will give the value of h .

Based on the kinetic parameter in Table 1, the pseudo second order kinetic model has accurately explained the experimental data. Both q_e calculated and the q_e experiments for pseudo second order are almost closed to each other compared to the pseudo first order. For pseudo second order, the value of q_e calculated for 10, 20 and 30 mg L⁻¹ were 11.99, 23.42 and 36.77 mg g⁻¹ respectively. These values are in good agreement with the value of the q_e experiment, 11.30, 20.65 and 35.59 mg g⁻¹ for 10, 20 and 30 mg L⁻¹ respectively. The R^2 value for the pseudo second order also close to the unity compared to the pseudo first which is very far from the unity. Hence, we can conclude that the pseudo second order kinetic model fitted well with all the experimental data which mean that the rate-limiting step for this adsorption process might be the chemisorption process. [23]. A similar finding was observed in the adsorption of Pb(II) ions from aqueous solution onto pine cone activated carbon [24].

Table 1. Adsorption kinetic parameters for Pb(II) adsorption on CFP

[Pb] mg L ⁻¹	q _e ^{exp} (mg g ⁻¹)	Pseudo-First-Order			Pseudo-Second-Order			
		q _e ^{cal} (mg g ⁻¹)	K ₁ (min ⁻¹)	R ²	h (mg/(g.min))	K ₂ (g/(mg.min))	q _e ^{cal} (mg g ⁻¹)	R ²
10	11.30	1.57	0.005	0.799	8.40	0.058	11.99	0.997
20	20.65	7.27	0.007	0.631	6.72	0.012	23.42	0.983
30	35.59	17.36	0.050	0.989	10.96	0.008	36.76	0.999

Conclusion

In this study, untreated CPF was characterized and tested as a potential new adsorbent for removal of Pb(II) ion from aqueous solution. It can be summarized that FTIR spectra analysis suggested that the CFP have a functional group that suits for Pb(II) ion adsorption. From the kinetic study, it can be confirmed that Pb(II) adsorption onto CFP is determined by chemisorption. The adsorption is very fast where the equilibrium was attained in less than 60 minutes. While, from the value of pH_{ZPC} and pH study, the adsorption can be carried out at pH 4 for optimum removal of Pb(II) ion from aqueous solution.

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