

# KINETIC AND ISOTHERM STUDIES OF LEAD ADSORPTION ONTO DURIAN LEAF POWDER

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## ABSTRACT

**The feasibility of citric acid modified durian leaf (CADL) to remove Pb(II) from aqueous solution was evaluated. CADL was characterized by using a Fourier transform infrared (FTIR) spectrometer to determine the effect of chemical modification on the functional groups of CADL. Parameters investigated in this study were pH, CADL dosage, initial Pb(II) concentration and contact time. Pb(II) adsorption onto CADL was best described by the pseudo-second-order model. The maximum monolayer adsorption capacity determined from Langmuir isotherm model was 16.64 mg/g.**

**Keywords:** Adsorption; Durian leaf powder; Isotherm; Kinetic; Pb(II).

## 1. INTRODUCTION

The presence of heavy metal such as lead, chromium, zinc and copper in aqueous solution has been highlighted over the past decade. Main contributors to water pollution that resulting from heavy metal come from waste disposal, mining, logging, transportation, shipping and aviation, agriculture and automobile industry (Ismail et al. 2013). One of the most leading metals that have been acknowledged is Lead (Pb). Lead has the ability to damage the physiology of human and another biological system. It tends to accumulate in food chain and persistence in nature due to its toxicity.

Various studies have been done to remove Pb(II) from the aqueous solution for example ion exchange method, membrane filter, chemical precipitation, activated carbon, coagulation, electrolysis, solvent extraction and adsorption technique (Reddy et al. 2010a). The Conventional method is an expensive method and often involves chemical usage that produces a large amount of sludge (Qaiser et al. 2009). The most promising method to remove lead in aqueous solution is adsorption. Adsorption is done by using various type of adsorbent including silica gel, activated alumina, activated carbons, zeolites, polymer and resins. Recently agricultural waste has been studied for its potentiality as adsorbent due to its availability and ease of operation (Zakaria et al. 2014).

Much agricultural waste use in the previous study for example Acacia leucocephala bark powder, Moringa oleifera bark, Neem leaves, olive tree pruning waste (Munagapati et al. 2010; Reddy et al. 2010b; Hanafiah et al. 2013; Calero et al. 2013). Study on Durian leaves has not yet being explored. However, there is few study that focuses on another part of Durian for removal of dyes including Durian rind, Durian peel and Durian seed (Mohammed et al. 2012; Hameed & Hakimi 2008; Ahmad et al. 2014).

This research was aimed at enhancing the adsorption capacity of durian leaf towards Pb(II) from aqueous solution by using citric acids. The carboxylic groups were introduced to the surface of durian leaf through esterification. Moreover, the effect of physicochemical parameters such as pH of Pb(II) solution, dosage and adsorption kinetics were also analyzed.

## 2. EXPERIMENTAL

### 2.1 Preparation of Durian Leaf Powder

Raw durian leaf was collected from the area located at Kampung Temiang, Muar, Johor, Malaysia. The leaf was rinsed with tap water and kept dry in an oven at 80 °C for overnight. The dried leaf was cut into small pieces and ground. The particle size 212 µM of the leaf powder were obtained and labelled as DL.

### 2.2 Preparation of Durian Leaf Modified Citric Acid

100 g of DL was placed in 2 L of 0.1 M NaOH and stirred at 300 rpm for 1 hour at 23 °C. The slurry was rinsed with distilled water to remove excess of base from leaves powder. The washed leaves powder was added with 1 M citric acid (CA) in the ratio of 1.0 g leaves and 7.0 mL CA. The CA treated durian leaf (CADL) was dried at 50 °C for overnight. CADL further washed by using distilled water at about 150-200 mL of distilled water per gram of CADL. This procedure was used to remove unreacted CA. The method used in this study was modified from Reddy et al. 2010a.

### 2.3 Characterization Technique

Determination of functional group present in the untreated Durian leaf (DLP) and CADL adsorbent were analyzed by using Fourier Transform Infrared Spectrometer. The adsorbent was scanned at 400-4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution.

### 2.4 Adsorption Study

The adsorption experiment was performed by using conical flask on water bath shaker set at 120 rpm and stirred for 90 minutes at room temperature. To achieve the optimum condition, studies were performed for different Pb(II) concentrations (10 to 30 mg L<sup>-1</sup>), pH (2.0–6.0) and CADL dosage from (0.02–0.10 g). After 90 minutes, the solutions were filtered and the concentration of Pb(II) in the filtrate was measured using AAS. The amount of Pb(II) adsorbed at equilibrium, q<sub>e</sub> (mg/g) was calculated by the following equation 1 and 2.

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

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

where C<sub>0</sub> and C<sub>e</sub> are initial and final Pb(II) concentrations after adsorption process respectively (mg L<sup>-1</sup>), V is the volume of Pb(II) solution (L), and m is the mass of adsorbent (g).

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of CADL

The FTIR spectra for untreated DL and CADL are presented in Figure 1. The formation of the sharp peak for C-O stretching band at  $1052\text{ cm}^{-1}$  after treatment with CA shows new additional carboxylic group. The intensity of the peak at  $1726\text{ cm}^{-1}$  for CADL is higher than before CA modified, indicating the result of CA esterification (Gong et al. 2006). The broad peak was observed at  $3272\text{ cm}^{-1}$  at CADL spectrum confirmed that the formation of carboxylic O-H and  $\text{-COOH}$  after CA modification.

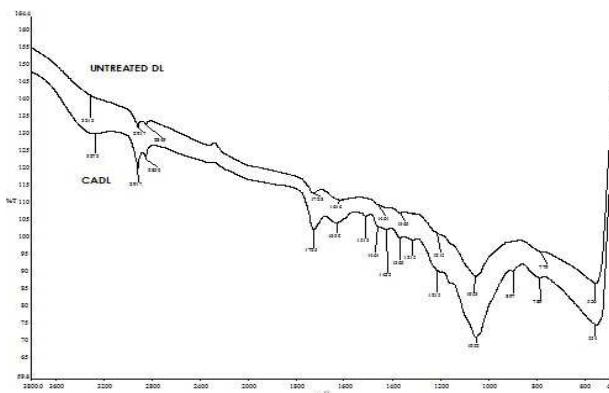


Figure 1: FTIR spectra of untreated CDL and CADL

#### 3.2 Effect of pH

Study on variable pH is important due to its significant effect on the interaction between metal ions and functional group at the adsorbent surface (Anayurt et al. 2009). Evaluation of pH effect onto adsorption of Pb(II) ion on CADL was done within the pH range 2 to 6 as shown in Figure 2.

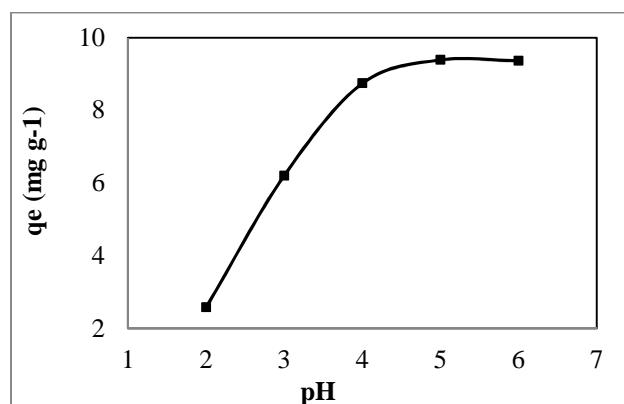


Figure 2: Effect of pH on Pb(II) ion adsorption (0.04 g adsorbent, 50 mL of  $10\text{ mg L}^{-1}$   $\text{Pb}^{2+}$  solution, 90 minutes at room temperature)

The results show by increasing the pH value from 2 to 5, adsorption capacity increased. But at pH 6, the adsorption capacity decreased due to the formation of a white precipitate. Thus, the adsorption experiments for Pb(II) removal using CADL were not performed at pH higher than

5. This trend also has been reported by other studies which indicated that adsorption efficiency of adsorbents was low at acidic pH and increases at higher pH values (Aksu 2001). At lower pH, free H<sup>+</sup> ions in the aqueous solution competed with Pb(II) ions for active sites present on CADL. Whereas by increasing the pH value, the competition between H<sup>+</sup> and Pb(II) ions decreased because the amount of H<sup>+</sup> ions is decreased. At higher pH value, the surface of adsorbent contains more negative surface charge resulting in the higher adsorption of Pb(II) ions by CADL (Qaiser et al. 2009). Therefore, based on these results, pH 4 was selected as for further experiments.

### 3.3 Effect of adsorbent dosage

Figure 3 shows the percentage removal of Pb(II) ion that evaluates the relationship between CADL dosage and Pb(II) adsorption. This study was done to distinguish the perfect dosage that will give the optimum Pb(II) removal and uptake capacity through the number of the binding sites which available to remove the metal ion at specified initial concentration. From the graph, the removal of Pb(II) ion increased over the increasing of the CADL dosage.

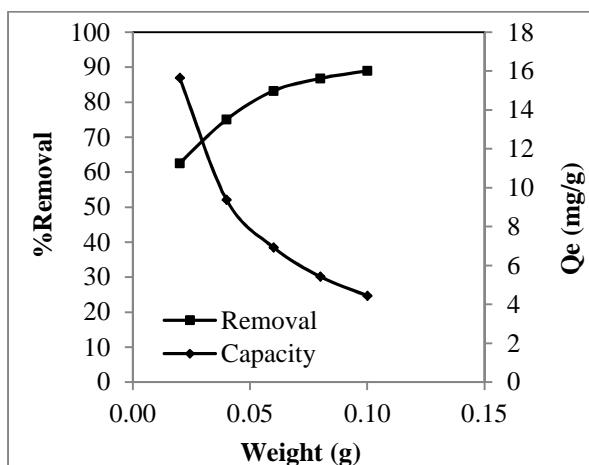


Figure 3: Effect of CADL dosage on Pb(II) ion adsorption (0.04 g adsorbent, 50 mL of 10 mg L<sup>-1</sup> Pb<sup>2+</sup> solutions, 90 minutes at room temperature)

In contrary, the uptake capacity per unit weight decreased as the dosage is increased. This can be explained by the increase in Pb(II) ion adsorption is due to the availability of the active site and surface area of adsorbent which increase directly with increasing of CADL dosage (Azouaou et al. 2010). Thus, dosage of 0.04 g was used in further studies.

### 3.4 Effect of initial concentration and contact time

Initial concentration effect on the adsorption studies was determined by using range between 10, 20 and 30 mg L<sup>-1</sup> of Pb(II) standard solution. This was done together with the study on the effect of contact time between the adsorbent, CADL and Pb(II) ion at each concentration. The range of time for the study was between 1 to 120 minutes. Figure 4 shows the relationship between the initial concentration and contact time of CADL.

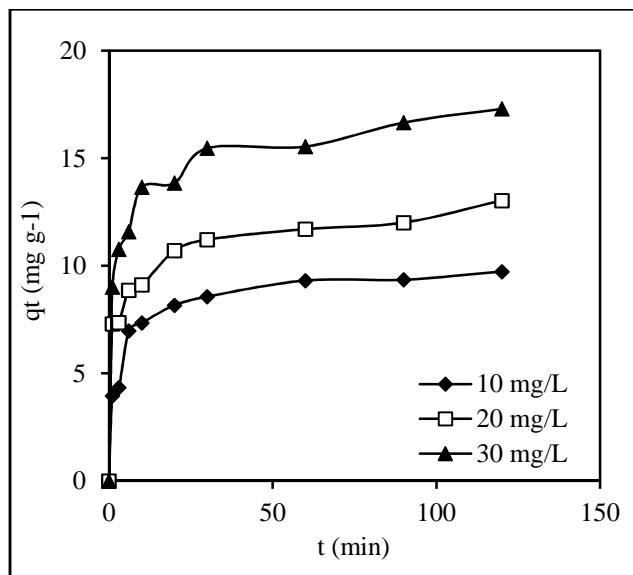


Figure 4: Effect of initial concentration and contact time on Pb(II) ion adsorption (0.04 g adsorbent, 50 mL of 10 mg L<sup>-1</sup> Pb<sup>2+</sup> solutions, 90 minutes at room temperature)

Based on the plot, three main phases were involved during the reaction. It was observed that the phases are rapid phases, slow phases and dynamic equilibrium phases. At first 10 minutes, rapid increases of Pb(II) ion removal was observed due to the availability of adsorption site. Much adsorption site was exposed for the adsorption to take place during this phase. As time increases, the slow phase was reached after 10 minutes until 60 minutes for 10 mg L<sup>-1</sup> Pb(II) ion concentration and become slower over time. This behaviour shows that the adsorption surface is limited since the available site have been accumulated by Pb(II) ion (Rahman & Othman 2014). It was observed that the adsorption process reached equilibrium at 90 minutes thus this study is conducted at 90 minutes of contact time.

### 3.5 Kinetic studies

Kinetic models were used to determine the rate of adsorption process and potentiality of rate-controlling step were proposed (Yuvaraja et al. 2014). To distinguish the mechanism and rate of adsorption on CADL, two kinetic models were used which is pseudo-first-order and pseudo-second-order model.

The formula of pseudo-first-order equation is shown in Equation (3):

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

The symbol of  $q_e$  indicates the amount of Pb(II) adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium while  $q_t$  means that the amount of Pb(II) adsorbed at a time (min) and  $k_1$  is the rate constant of adsorption process ( $\text{min}^{-1}$ ) of the pseudo-first-order. The values of  $k_1$  and  $q_{e,\text{cal}}$  were calculated from the slopes ( $k_1$ ) and intercepts ( $\log q_e$ ) of the plots of  $\log (q_e - q_t)$  vs.  $t$  (Figure 5), respectively, and are presented in Table 1. The calculated  $q_e$  values obtained from this

kinetic model did not satisfy the experimental one. Therefore, the adsorption process did not follow the pseudo-first order.

The second adsorption kinetic was analyzed by using pseu-do-second-order kinetic model Equation (4):

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4)$$

Where  $q_e$  and  $q_t$  represent the amount of Pb(II) ( $\text{mg L}^{-1}$ ) at equilibrium and time ( $t$ ) respectively while  $h$  is the initial adsorption rate, ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) and  $k_2$  is the rate constant of pseudo-order adsorption ( $\text{g mg}^{-1} \cdot \text{min}^{-1}$ ). The pseudo-second-order plot is shown in the Figure 6.

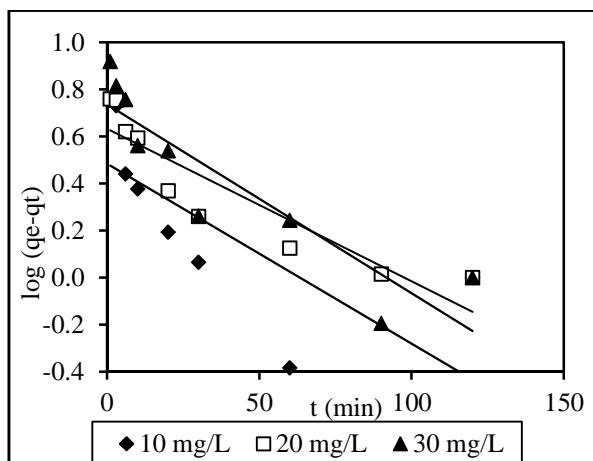


Figure 5: Pseudo-First-Order Plot on Pb(II) adsorption onto CADL

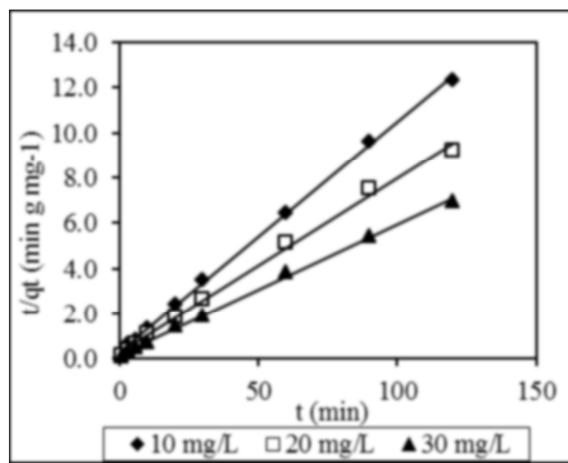


Figure 6: Pseudo-second-order plot on Pb(II) adsorption onto CADL

The value of  $R^2$  and experimental  $q_e$  is tabulated in Table 1. The correlation coefficient,  $R^2$  value for CADL at various concentration were in between 0.9992 to 0.9977 which is more

agreeable compared to pseudo-first-order model. Higher  $R^2$  value shows that there is smaller gap between experimental and calculated  $q_e$  based on the table. This indicates that the pseudo-second-order is applicable in explaining that the adsorption process where due to chemical reaction (Qaiser et al. 2009).

### 3.6 Isotherm studies

Isotherm studies were done to analyze the connection between adsorbate and adsorbent at equilibrium and the maximum adsorption capacity of adsorbent. Common isotherm model that is widely used is Langmuir and Freundlich models. Adsorption isotherms are numerical models that portray the dissemination of the adsorbate species among liquid and solid phases depends on the homogeneity or heterogeneity of solid surface assumptions models which is Langmuir or Freundlich isotherm model (Kalalagh et al. 2011).

Table 1: Pseudo-first-order and pseudo-second-order parameter at various Pb(II) concentration

[Pb] mg L <sup>-1</sup>	Pseudo-First Order			Pseudo-second Order			$q_e$ , exp (mg/g)
	$q_{e,cal}$ (mg g <sup>-1</sup> )	$K_1$ (min <sup>-1</sup> )	$R^2$	$h$ (mg/(g.min))	$K_2$ (min <sup>-1</sup> )	$q_{e, cal}$ (mg/g)	
10	3.0528	0.0977	0.5838	2.9568	0.0304	9.8619	0.9992 9.35
20	4.2954	0.01497	0.8318	3.7594	0.0225	12.9199	0.9965 12.00
30	5.4488	0.0184	0.8174	5.5066	0.0183	17.3611	0.9977 16.65

Table 2: Isotherm parameters for Pb(II) biosorption onto CADL at a constant temperature; (30 °C)

Langmuir			Freundlich			
$q_{exp}$ (mg g <sup>-1</sup> )	$q_{max}$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R^2$	$K_F$ (mg g <sup>-1</sup> )	n	$R^2$
15.28	16.64	0.38	0.9973	5.5297	3.0175	0.9778

Langmuir model has been proposed by Langmuir (1918) which their assumption on the metal ion uptake occurs on a homogenously on surface by monolayer adsorption. This happens with the no interaction with adsorbed ions. Equations 5 arise from the linearization are as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad (5)$$

Where  $q_e$  and  $C_e$  are Pb(II) uptake on the biosorbent (mg g<sup>-1</sup>) and Pb(II) concentration in the solution (mg L<sup>-1</sup>) at equilibrium respectively. As  $q_{max}$  is the maximum biosorption capacity (mg g<sup>-1</sup>) and  $b$  is the Langmuir constant (L mg<sup>-1</sup>). The plot of  $C_e/q_e$  versus  $C_e$  was used to analyze the  $b$  and  $q_{max}$  from intercept and slope respectively. The Langmuir constant is related to the free energy of sorption constantly (Rahman & Othman 2014). The Langmuir model depends on the presumption that a fixed number of adsorption that is accessible on the surface of the adsorbent and every site can take up the most of one particle, where the adsorption energy is static (Kalalagh et al. 2011).

As stated in Table 2,  $R^2$  for Langmuir plot is 0.9973 which indicates the adsorption studies fit with this model very well. The value of  $q_{max}$  that has been evaluate is 16.64 mg g<sup>-1</sup>.

Freundlich isotherm models proposed by Freundlich (1906) assume that the empirical equation is established on the adsorption on heterogenous surface. Evaluation of Freundlich isotherm is given by using equation 6 as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Where the  $k_f$  is the rate constant indicating that it is the maximum adsorption capacity (mg/g) and  $n$  is the adsorption intensity.  $n$  value is referred to the favourablity of the adsorption. If the  $n$  value is within the range of 1 to 10, it is classified as favourable adsorption (Chantawong et al. 2003).

However, value of  $R^2$  shows in Table 2 for Freundlich model is lower than the  $R^2$  obtained in Langmuir model's evaluation. This is made clear that Freundlich model didn't fit with the experimental data very well. The results indicates that the connection between amount of metal ion adsorbed and its equilibrium concentration is not been described properly by using this models.

#### 4. CONCLUSION

This research successfully produced a new potential adsorbent of CA modified durian leaves powder which has an ability to remove Pb(II) from aqueous solution. Based on data analysis obtained, the optimum condition for adsorbent dosage are (0.04 g), initial concentration (10 mg/L) and 90 minutes. The equilibrium data was fitted well with Langmuir isotherm whereas the kinetics was best described by pseudo-second-order rate model.

#### 5. ACKNOWLEDGEMENT

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