

The Removal of Pb(II) and Cr(VI) From Aqueous Solution by Longan Skin Adsorbent

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Abstract: This study investigated the use of longan skin, an agricultural waste, as an adsorbent for removing Pb(II) and Cr(VI) from aqueous solution. The results indicated that the maximum removal efficiency of Pb(II) and Cr(VI) reached 99% at solid-liquid density of 5 g/L, initial concentration of 50 mg/L, and shaking speed of 100 rpm. The adsorption isotherm and kinetic of Pb(II) and Cr(VI) removal was the best described by Freundlich model and Pseudo - second order with the relative coefficient over 0.97 and adsorption capacity 56.8 mg/g and 18.5 mg/g, respectively. Based on the experimental results, the study suggested that longan skin may be used as a low cost adsorbent for removing Pb(II) and Cr(VI) from aqueous solution.

Keywords: longan skin, Pb(II), Cr(VI), adsorption

1. INTRODUCTION

Untreated industrial effluents, particularly from electroplating, surface treatment processes, are the main sources of heavy metals causing contamination of the water resources. The presence of heavy metals such as Pb (II), Cr(VI) at a high level in water pose a threat to both human beings and animals. The adsorption is the common method for removing heavy metal ions in aqueous solution. Traditionally, ion resins and synthetic materials are chosen. However, the recent researches have indicated that some types of dried biomass such as longan skin [1-3], orange peel [4], lemon peel [5], fruit peels [6], banana peel [7], after being treated with a simple method, could be used as a low cost adsorbent material. The reason is that fruit peels and skins often contain such functional groups as $-\text{CO}_2\text{H}$, $-\text{OH}$, $\text{N}-\text{H}$, $\text{C}-\text{H}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$, which can form ligand when loaded with heavy metal ions and holds on the surface.

Longan is a tropical fruit widely cultivated in Vietnam. The fruit skin and seed are considered waste result from the longan fruit processing. This study investigated the use of longan skin, as an adsorbent for removing Pb(II) and Cr(VI) from the aqueous solution under the effects of contact time, initial pH, solid-liquid density, and shaking speed.

2. EXPERIMENTAL PROCEDURES

1. Adsorbent preparation

A sample of longan skin were collected from a craft village in Hung Yen province in Vietnam. The raw longan skin was washed, air dried, ground and sieved to obtain particles sized within a range of 600 μm - 2000 μm . The volume and inner diameter of the pore were measured at about 0.001694 cm^3/g and 224.5 A° (Figure 1). The obtained material of the longan skin was washed with boiled deionized water to remove color and dried at 80 $^\circ\text{C}$ to yield the adsorbent (hereinafter referred as to DLS in this article) for the batch adsorption experiment. Typical functional groups detected on the surface of the adsorbent include $-\text{CO}_2\text{H}$, $-\text{OH}$, $\text{N}-\text{H}$, $\text{C}-\text{H}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$ (Figure 2).

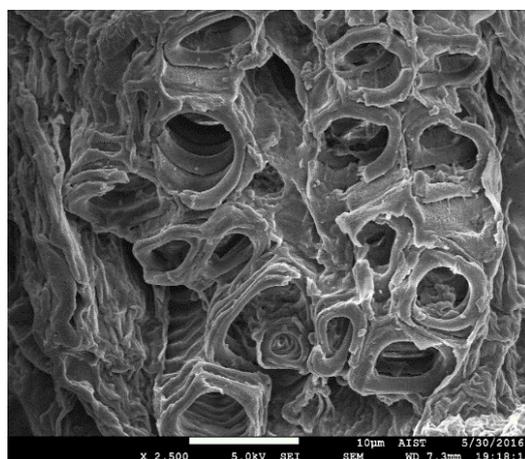


Fig 1: SEM image of the DLS

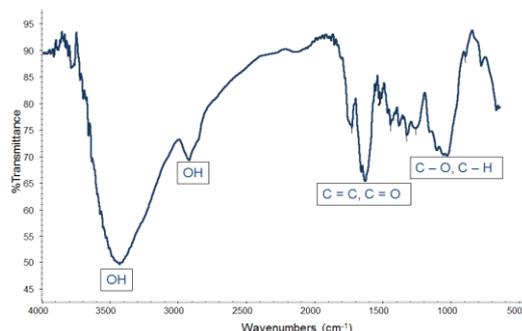


Fig 2: Result of FTIR analysis of DLS

2. Chemicals and metal solution

All chemicals used in this work were of analytical grade produced by Merck (Germany). The Pb(II) and Cr(VI) stock solution with the concentration of 1 g/L was prepared by dissolving the desired amounts of $Pb(NO_3)_2$ and $K_2Cr_2O_7$ respectively in deionized water. The working solutions with the concentration of 50 mg/L were obtained by diluting the stock solutions with deionized water. The initial pH of Pb(II) and Cr(VI) solutions were adjusted with NaOH and HNO_3 solutions.

3. Batch experiment

The batch adsorption experiments were conducted at 25°C. A measured volume of the working solution of either Pb(II) or Cr(VI) and a desired amount of the DLS were placed in the 100 mL conical flask with the phase ratio of 200 mL/g and agitated at a speed of 100 rpm. After finishing each batch and phases separation by paper filtration, pH of the experimental solutions was measured to determine pH at the equilibrium by Toledo pH meter. The Pb(II) concentration in the experimental solutions were analyzed by using ICP-OES (Ultima 2, Horiba). The concentrations of Cr(VI) ions in the solution was determined spectrophotometrically at 540 nm using 1,5-diphenylcarbazide as the complexing agent. The Pb(II) and Cr(VI) removal efficiency is calculated based on the mass balance equation as follows:

$$E(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Where:

E: Pb(II) and Cr(VI) removal efficiency (%)

C_o : Initial Pb(II) or Cr(VI) concentration (mg/L)

C_e : Pb(II) or Cr(VI) concentration remains in the adsorbed solution at the equilibrium (mg/L)

C_{ad} : the amount of Pb(II) or Cr(VI) adsorbed on the DLS adsorbent at the equilibrium (mg/g)

The accuracy of the efficiency calculation based on the different C_o , total of C_e , Pb(II), Cr(VI) adsorbed on the DLS adsorbent at the equilibrium C_{ad} (mg/L) was less than 5%.

3. RESULTS AND DISCUSSIONS

1. Effect of initial pH

In this study, pH of the experimental solutions was carried out in the range of 1.5 – 5.0 for Pb(II) and 0.75

to 8.0 for Cr(VI) in order to prevent any formation of precipitation of Pb(II) and Cr(VI) hydroxides, which may occur in a higher pH condition. The effect of initial pH on Pb(II) removal is presented in Figure 3.

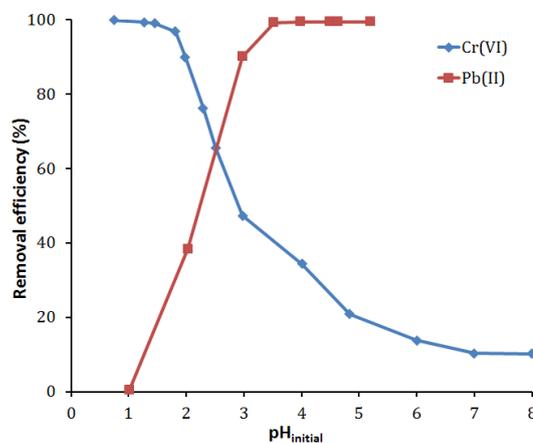


Fig 3: Effect of initial pH on Pb(II) and Cr(VI) removal (initial Pb(II) and Cr(VI) concentration 50 mg/L, contact time 300 minutes, solid-liquid density 5 g/L, shaking speed 100rpm, DLS particle sizes 600-1000 μm)

The results show a contrasting effect of pH on the Pb(II) and Cr(VI) removal. The Pb(II) removal efficiency increased rapidly from 0.3% to 99.3% as pH rose from 1.0 to 3.5, and reach a stable maximum of 99% within the pH range of 3.5-5.2. Whereas, the Cr(VI) removal efficiency reach the maximum of 99.4% within the pH range of 0.75-1.5, and decreased from 99.4% to 33.4% as pH increased from 1.5 to 4.0. At the initial pH of 8.0, the removal efficiency was 10.3%. In the other words, the initial pH ranges for achieving the optimal removals of Pb(II) and Cr(VI) were 3.5-5 and 0.75-1.5 respectively. This observation may be explained by the influence of pH on the existence and mobility of Pb(II) and Cr(VI) in the solution, which in turn impeded the contact among Pb(II), Cr(VI) ions and functional groups on the adsorbent, such as $-CO_2H$, $-OH$, $N-H$, $C-H$, $C=O$. These functional groups carried a positive charge when being protonated in a low pH condition and negative charge at a higher pH condition. At the low pH condition, the OH group is activated by H^+ to form OH^+ , which easily attracts Cr(VI) mainly existing in $HCrO_4^-$ form or Pb(II) through the H^+ exchanging in the solution. However, at the pH higher than 1.5, almost all $Cr_2O_7^{2-}$ were converted into $Cr_2O_7^{2-}$ and CrO_4^{2-} . Besides, the NH functional groups on the surface of the DLS adsorbent also plays a role of an active site. This group comes in contact and holds Pb(II) and Cr(VI) on the surface of the adsorbent by electrostatic coordinate bonding [8].

2. Effect of contact time

Contact time is one of the most important factors in the batch adsorption process. Initially, the adsorption rate increased rapidly. The second stage represented a slower progressive adsorption. The maximum removal efficiency of Pb(II) and Cr(VI) was reached 99.5% and 99.8% after 60 minutes and 300 minutes, respectively (Figure 4). A further increase in contact time did not show significant change in the heavy metal concentrations at equilibrium. The mechanism of the solute-to-solid transfer includes diffusion through the fluid film around the adsorbent particles and diffusion through the pores to the internal adsorption sites. At the initial stages of adsorption, the concentration gradient between the film and the availability of the pore sites are large, and therefore the rate of adsorption is faster. The rate of adsorption however decreases at the later stages probably due to the slower pore diffusion of the solute ion into the bulk of the adsorbent. This result was found to similar to Meilia Innes Kurniawan [1], Florenlya [2].

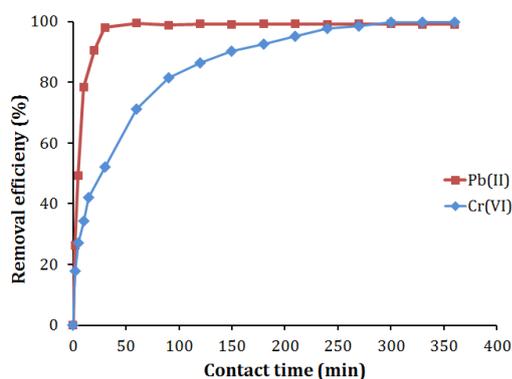


Fig 4: Effect of contact time on Pb(II) and Cr(VI) removal (initial pH 4.0 for Pb(II) and 1.5 for Cr(VI), initial concentration 50 mg/L, shaking speed 100 rpm, DLS particle size 600-1000 μ m, solid-liquid density 5 g/L)

3. Effect of solid-liquid density

The results of relationship between the solid-liquid density and the removal efficiency of Pb(II) and Cr(VI) are shown in Figure 5. The removal efficiencies increased rapidly from 60% to 99.5% for Pb(II) and from 18% to 99.8% for Cr (IV) when solid-liquid density increased from 0.5 g/L to 3.0 g/L for Pb(II) and from 0.5 g/L to 5.0 g/L for Cr (VI). These results are expected because the increase in adsorbent dose leads to the greater surface area and the number of active sites. However, at the higher solid-liquid density, the equilibrium uptake of metal ions did not increase significantly with increasing DLS dosages. Such

behavior is expected due to the saturation level attained during the adsorption process.

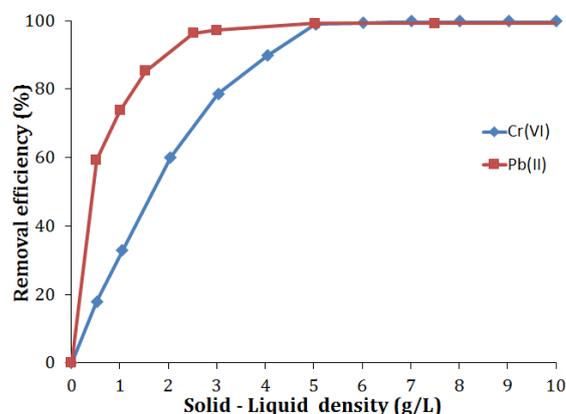


Fig 5: Effect of solid-liquid density on Pb(II) and Cr(VI) removal (initial pH 4.0, contact time 60 minutes for Pb(II), initial pH 1.5 contact time 300 minutes for Cr(VI), initial concentration of 50 mg/L, solid - liquid density 5 g/L, shaking speed 100 rpm, DLS particle sizes of 600-1000 μ m)

4. Effect of shaking speed

As the results indicated in Figure 6, the maximum removal efficiencies for the Pb(II) and Cr(VI) were achieved at shaking speed in the range of 100 - 200 rpm, suggesting that the diffusion of solid and liquid phases were optimal within this range. When the shaking speeds were lower than 100 rpm, the removal efficiencies for the Pb(II) and Cr(VI) declined, indicating that the contact between liquid and solid phase was not sufficient to obtain optimal adsorption.

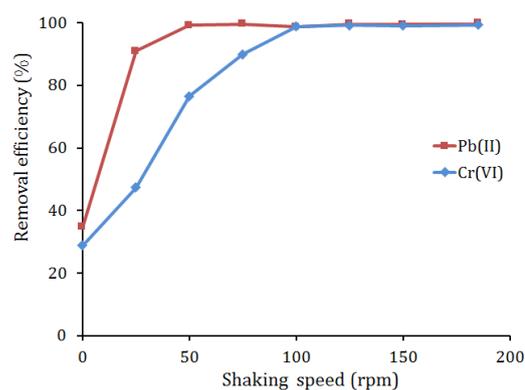


Fig 6: Effect of shaking speed on Pb(II) and Cr(VI) removal (initial pH 4.0, contact time 60 minutes for Pb(II) and 1.5 contact time 300 minutes for Cr(VI), initial concentration 50 mg/L, solid-liquid density 3 g/L and 5 g/L, DLS particle sizes 600-1000 μ m)

5. Effect of longan skin particle sizes

The actual adsorption efficiency depends on the surface area and the number of active sites of adsorbent. When

the particle size is larger the total area surface is smaller. However, the results shown in **Figure 7** suggested that the removal of lead and chromium ions did not depend on the particle size in the range 600-2000 μm . Despite a significant difference in the particle sizes of 600 - 1000 μm and 1000 - 2000 μm , the removal efficiencies for these ions were very similar.

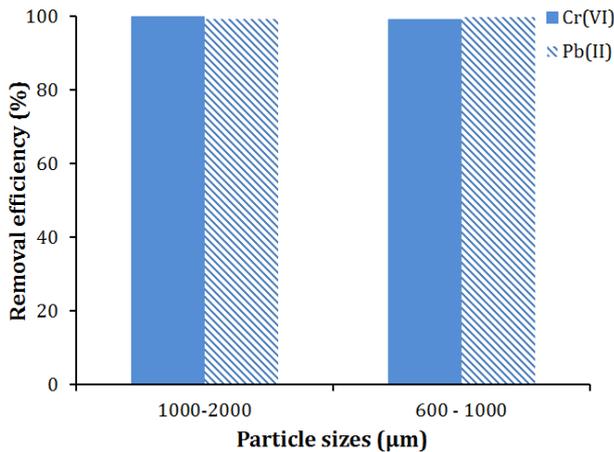


Fig 7: Effect of particle size of DLS adsorbent on Pb(II) and Cr(VI) removal (initial pH 4.0, contact time 60 minutes for Pb(II) and initial pH 1.5 and contact time 300 minutes for Cr(VI), initial concentration 50 mg/L, shaking speed 100rpm, solid-liquid density 3.0 g/L and 5.0 g/L)

6. Adsorption isotherm

The linearized Langmuir adsorption isotherm equation which is valid for monolayer sorption onto a surface with a finite number of identical sites is presented as follows:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{b \cdot q_m} \quad (2)$$

Where:

C_e : the equilibrium concentration of Pb(II) or Cr(VI) in solution (mg/L),

q_e : the amount Pb(II) or Cr(VI) adsorbed at equilibrium (mg/g),

q_m : the theoretical maximum adsorption capacity (mg/g)

b : the Langmuir constant (L/mg).

The linear plot of $\frac{C_e}{q_e}$ versus $\frac{t}{q_e}$ with correlation coefficient R^2 over 0.98 for Cr(VI) and 0.84 for Pb(II) indicates the applicability of Langmuir adsorption isotherm (**Figure 8**).

Freundlich adsorption isotherm adopts multilayer adsorption on heterogeneous surfaces. Linearized form of the Freundlich equation is given by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} C_e \quad (3)$$

Where:

q_e : the amount of Pb(II) or Cr(VI) adsorbed at equilibrium time (mg/g),

C_e : the equilibrium concentration of Pb(II) or Cr(VI) in the solution (mg/L),

K_f : the equilibrium parameter (mg/g),

n : an empirical parameter,

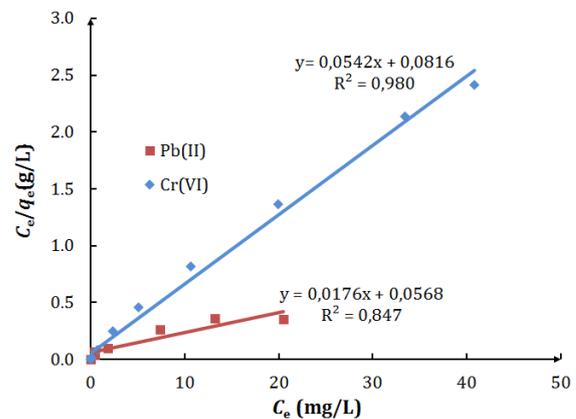


Fig 8: Langmuir isotherm of Pb(II) and Cr(VI) removal by longan skin

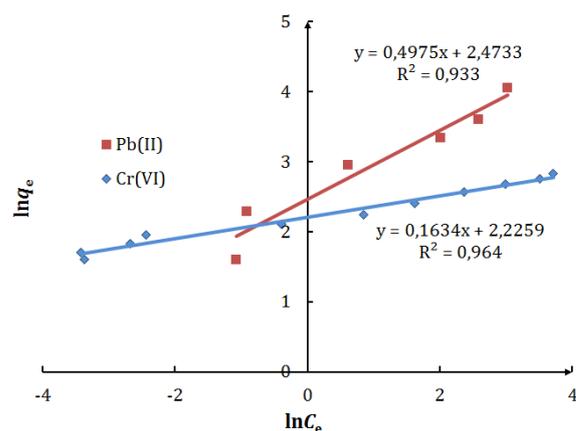


Fig 9: Freundlich isotherm of Pb(II) and Cr(VI) removal by using longan skin

Comparing the R^2 between Langmuir and Freundlich models for Cr(VI), it could be realized that R^2 calculated at 0.98 and 0.93 were very similar for both models. Meanwhile, for Pb(II) adsorption, R^2 of Freundlich model of Pb(II) was 0.96, higher than Langmuir model

0.84. This may suggest that the Cr(VI) adsorption adhered to both Langmuir and Freundlich models, while the Pb(II) adsorption followed well into Freundlich model better than Langmuir model. The adsorption capacity of DLS for Pb(II) and Cr(VI) was 56.8mg/g and 18.5 mg/g, respectively.

Table 1: Adsorption isotherm parameter of Pb(II) and Cr(VI) by DLS.

Metalions	Langmuir isotherm		
	q_m (mg/g)	b (l/mg)	R^2
Pb(II)	56.8	0.31	0.847
Cr(VI)	18.5	0.66	0.980
Metalions	Freundlich isotherm		
	K_F	n	R^2
Pb(II)	11.86	2.010	0.933
Cr(VI)	9.26	6.120	0.964

7. Adsorption kinetic

The rate constant K_1 for the adsorption of Pb(II) and Cr(VI) by using DLS was studied by Lagergren rate equation [9] for initial Pb(II) and Cr(VI) of 50 mg/L. Pseudo-first-order rate expression of Lagergren equation:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.203} \quad (4)$$

Where:

q_e : The amount of Pb(II) or Cr(VI) adsorbed at the equilibrium (mg/g)

q_t : The amount of Pb(II) or Cr(VI) adsorbed at time 't' (min), respectively (mg/g)

K_1 : The Pseudo-first-order rate constant (min^{-1}).

The K_1 and correlation coefficient R^2 were calculated from the slope of the linear plot of $\log(q_e - q_t)$ versus 't' at different time intervals. The K_1 and R^2 of DLS are shown in Table 2.

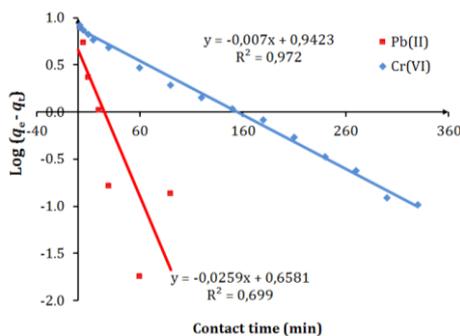


Fig 10: Pseudo – first – order of Pb(II) and Cr(VI) adsorption by using DLS

The Pseudo-second-order rate expression is:

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \quad (5)$$

Where:

K_2 is the Pseudo-second-order rate constant (g/mg.min).

The calculation from the slope and intercept of the plot

$\frac{t}{q_t}$ versus time 't' was almost linear shown in **Figure 11**.

The values of K_1 , K_2 and R^2 of DLS are shown in Table 2

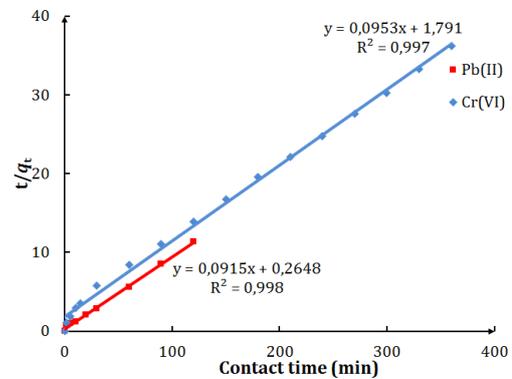


Fig 11: Pseudo – second – order of Pb(II) and Cr(VI) adsorption by DLS

With correlation coefficient R^2 of Pseudo –second order of both Pb(II) and Cr(VI) were 0.998 and 0.997 higher than 0.69 and 0.97 of Pseudo – first order. In addition, from Table 2, it can be seen that the experimental value of $q_{e,exp}$ is not in a good agreement with the theoretical value calculated (q_{e1}) from Eq. (4). Therefore, the Pseudo-first-order model is not suitable for modeling the adsorption of Pb(II) and Cr(VI) onto DLS. It is suggested that the adsorption kinetic of Pb(II) and Cr(VI) are followed the Pseudo – second order.

Table 2: Adsorption kinetic parameter of Pb(II) and Cr(VI) by DLS.

Metal ions	$q_{e,exp}$ (mg/g)	Pseudo -first order		
		k_1 (min^{-1})	q_{e1} (mg/g)	R^2
Pb(II)	10.57	0.0596	4.551	0.699
Cr(VI)	9.95	0.0161	8.756	0.972
Metalions	$q_{e,exp}$ (mg/g)	Pseudo - second order		
		k_2 (min^{-1})	q_{e2} (mg/g)	R^2
Pb(II)	10.57	0.032	10.929	0.998
Cr(VI)	9.95	0.0051	10.493	0.997

8. FTIR and SEM

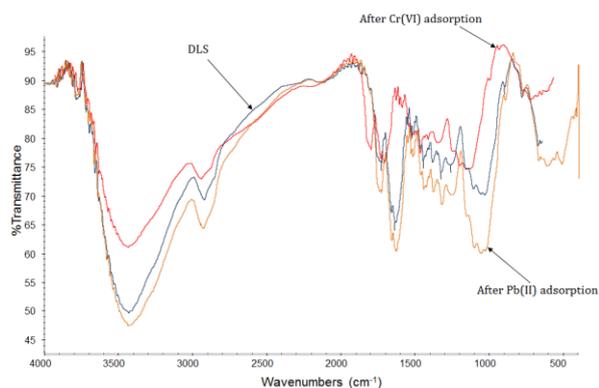


Fig 12: FTIR analysis of DLS before and after Pb(II) and Cr(VI) adsorption.

The FTIR analysis results (**Figure 12**) shows the different peak heights for the adsorbent before and after Pb(II) and Cr(VI) adsorption. This graph described the adsorption mechanism of Pb(II) and Cr(VI) at the low pH condition. As discussed in the previous parts of this article, DLS adsorbent contains various functional groups such as OH, NH, CHO, playing the role of active sites, which directly contact with Pb(II) and Cr(VI).

SEM images (**Figure 13**) shows structure of the DLS adsorbent before and after Pb(II) and Cr(VI) adsorption. It is obvious that the adsorbent had a hollow structure with the pore diameter measured at 224.536 Å, larger than the diameter of both Pb(II) and Cr(VI) of 133 Å and 52 Å respectively. Therefore, it could be said that Pb(II) and Cr(VI) was adsorbed not only on the surface of the adsorbent through combining with the NH or OH functional groups, but also inside the pores.

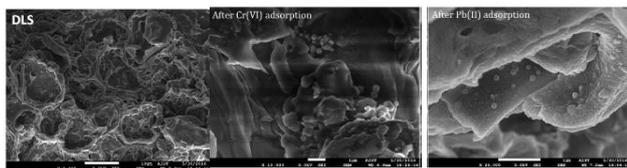


Fig 13: SEM images of DLS before and after Pb(II) and Cr(VI) adsorption.

4. CONCLUSIONS

According to the results presented in this study, according to the results obtained in this study, some conclusions can be recommended as follows:

- Longan skin can be used as a low-cost adsorbent material for Pb(II) and Cr(VI) removal from an aqueous solution.

- The Pb(II) removal was found to highest at initial pH 3.5 -5.2, contact time 60 minutes, solid-liquid density of 3.0 g/L, shaking speed 100 rpm with the adsorption capacity of 56.8 mg/g.
- The Cr(VI) removal efficiency was found to highest at initial pH 1.5, contact time 300 minutes, solid-liquid density of 5 g/L, shaking speed 100rpm with the adsorption capacity of 18.5 mg/g
- The adsorption isotherm for Cr(VI) was found to follow both Langmuir and Freudlich with the correlation coefficient R^2 over 0.98 and 0.96, respectively.
- The adsorption isotherm for Pb(II) was found to the best described by Freudlich model with the correlation coefficient R^2 0.93.
- The adsorption kinetic of Pb(II) and Cr(VI) was the best described by Pseudo - second order with correlation coefficient R^2 over 0.99.

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- Environmental monitoring

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