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**Journal of Chemical and Pharmaceutical Research, 2015, 7(9):100-106**

**Research Article**

**ISSN : 0975-7384**
**CODEN(USA) : JCPRC5**

# Removal of Pb(II) ions by using Papaya (*Carica papaya* L) leaves and Petai (*Parkia Speciosa* Hassk) peels as biosorbent

**Tan Suyono[1], Mhd. Adhil Yuser[2], Edison Munaf[2], Hermansyah Aziz[2], Djong Hon Tjong[3] and Rahmiana Zein[2*]**

*[1]Department of Tropical Medicine, Faculty of Medicine, Prima Indonesia University, Medan, Indonesia*
*[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Padang, Indonesia*
*[3]Department of Biology, Faculty of Mathematics and Natural Sciences, Andalas University, Padang, Indonesia*

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## ABSTRACT

*The biosorption of Pb(II) ionsfrom aqueous solutions using Papaya (Carica papaya L) leavesand Petai (Parkia speciosa Hassk) peels activated with $HNO_3$ 0,01 mol/Lwas studied in batch method. The optimum conditions forbiosorption of Pb(II) ions at pH 4.0, initial concentration 5400 mg/L using Papaya leaves and pH 5.0, initial concentration 590 mg/L using Petai peels. While optimum contact time 15 min, biosorbent mass 0.1 g for both biosorbent with biosorption capasity (Q) of Pb(II) ions at 284.35 mg/g and 36.01 mg/grespectively. The biosorpstion data follow Langmuir isotherm models by using Petai peels and follow Freundlich isotherm by using Papaya leaves. The concentration Pb(II) ions after biosorption were measured by using Atomic AbsorptionSpectrofotometer (AAS), while the characterisation biosorbent performed using Scanning Electron Microscope (SEM) and Fourier Transform Infra Red Spectroscopy (FTIR). FTIR analysis showed the hydroxyl and carboxyl functional groups have a role in the biosorption process of Pb(II) ions.*

**Keywords**: Biosorption, Pb(II), Papaya (*Carica papaya* L) leaves, Petai (*Parkia speciosa* Hassk) peels.

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## INTRODUCTION

Water pollution due to heavy metals is one of the most significant environmental problems.Heavy metals are non-biodegradable and can accumulate through the food chain so that it becomes a threat to aquatic life, plants, animals and human health [1-2]. Lead is one of the toxic heavy metals even at low is concentration [3]. According to WHO, the maximum limited of lead in water is 0.05 mg/L [4-5] and the agricultural sludge was 420 mg/L [6]. The main sources of lead into the environment are derived from baterai manufacturing, metal plating, metallurgi process, paint, printing process and other [7-8].

Some techniques used to reduce the content of heavy metals in waters such as ion exchange, precipitation chemistry, engineering memberan, adsorption [9-11], but these techniques produce toxic sludge and not environmentally friendly. The other alternative to reduce heavy metal contamination is by biosorption method. Biosorption by using biomaterials or agricultural waste such as soursop seed [12], manggosteen fruit shell [13], baobab shell [14], honeycomb [15], and others have been tested can be used to decrease toxic pollutants in wastewater. In addition low-cost and easy to be obtained, using of biomaterials as biosorbent to decrease the organic solid waste.

Biomaterials utilized as biosorbent because they contain functional groups such as hydroxyl, carboxyl, the amino group wherein the functional groups can binding to metal ions [11]. Based on previous research, Papaya leaves and Petai peels are used as biosorbent to decrease concentration of ions Pb(II) in water pollution.

## EXPERIMENTAL SECTION

### Chemicals and Equipments

All the necessary chemicals $Pb(NO_3)_2$, NaOH, $HNO_3$, $CH_3COOH$, $CH_3COONa$, $NH_4OH$, $NH_4Cl$ are analytical grade and obtained from E-Merck (Germany) and distilled water from laboratory made. The equipments used in this study are the cruiser (Fritsch, Germany), pH meter (Metrohm), analytical balance (Kern & Sohn GmbH), a rotary shaker (Edmund Buhler Tubingen 7400), AAS (spectraAA-240 VARIANT), Oven (Memmert) , FTIR (Thermo Scientific NICOLET is10), SEM (Hitachi S-3400) and other laboratory glassware.

### Preparation of Biosorbent

Papaya leaves and Petaipeels was collected, washed with deionized water, air dried and then grounding using mortal grinder. The powder was activated by soaking 20 g biomass in excess of 80 mL $HNO_3$ 0.01 M for 3 h, followed by washing thoroughly with deionized water and then air-dried. The resulting pale brown powder can be stored for a long time.

### Batch Adsorption

Powder of Papaya leaves and Petai peels was entered into 10 mL solution containing Pb(II) ions, and stirred using a shaker for several minutes. The effect of pH of the solution, initial concentration, contact time, mass of bioserbent were studied. After sorption, the mixture was filtered through filter paper. The concentration of Pb(II) in solution after equilibrium was determined by Atomic Absorption Spectrophotometer (AAS).

The amount of adsorb metal ions (adsorption capacity, Q) was obtainedusing the following equation:

$$q = \frac{(C_o - C_e)\,V}{m} \qquad (1)$$

Where "Co" and "Ce" were initial and equilibrium metal ions concentration in solutions (mg/L),respectively; "V" was volume of the solution (L); "m" was the amount of biomass (g).

## RESULTS AND DISCUSSION

### Effect of pH Solution

pH is an important parameter in biosorption of Pb(II). pH significantly affect the amount of adsorbed metal ions [16]. $H^+$ ions will compete with metal ions for binding to active site of adsorbent. Fig. 1 shows the adsorption of Pb(II) ions using Papaya leaves and Petai peels. Biosorption process performed on pH 3-8. Adsorption capacity of Pb(II) is low at pH 3. At low pH, biosorbent surface surrounded by hydronium ions ($H_3O^+$), so there is competition between the metal ions with hydronium ions ($H_3O^+$) to bind the active site of biosorbent.The increase in pH causes competition between hydronium ions ($H_3O^+$) and metal ions decrease. Biosorbent surface becomes more negative and metal ions is more easily adsorbed because there is attraction between the metal ions with functional groups that exist in biosorbent [15,17]. pH> 5begin to form $Pb(OH)_2$. The optimum pH value = 4 by using Papaya leaves and pH = 5 using Petai peels and was used in all the further experiment variable.

### Effect of Initial Concentration

Effect of Pb (II) ion concentration on sorption into the skin Petai papaya and studied by varying the concentration of metal ions. Biosorption results at various concentrations shown in Fig. 2. The sorption capacity increased with increasing concentration of Pb(II) ions. At low concentrations, less amount of metal ions is bound into active site so availability vacancy at biosorbent surface. Increasing concentration, causing more collisions between metal ions and biosorbent. The existence of this collision causes attractive force of metal ions and large active side and adsorption capacity increased [16].The sorption capacity decreased after optimum concentration achieved. This is due to the lack of availability of active side of biosorbent to bind metal ions. From the result Fig. 2. show that powder Papaya leaves having a hight sorption capasity compare withand Petai Peels.

### Effect of Contact Time

Fig. 3 shows the effect of contact time on metal ions adsorption. Effect of contact time were conducted to determine the optimum time uptake of Pb(II) by using Papaya leaves and Petai Peels.The optimum time for adsorption of Pb(II) obtained 15 minutes for the both biosorbent. Adsorption capacity of Pb(II) decreased with increasing contact time due to the release of metal ions that have been re-bound to the active site of biosorbent.

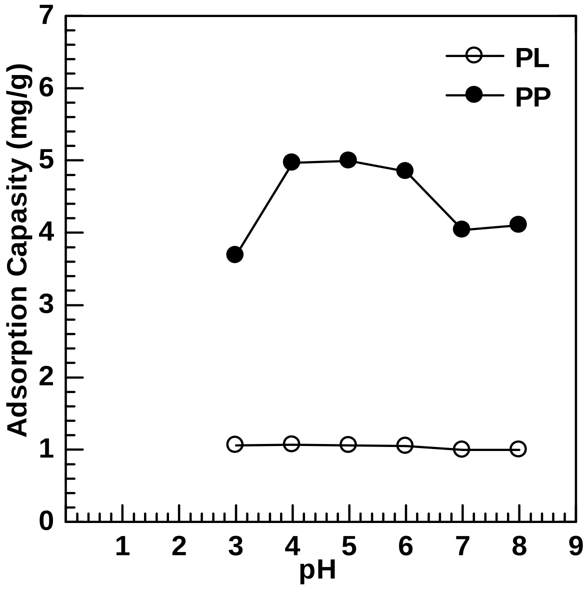


**Fig. 1. Effect of pH of solution on the adsorption capasity of Pb(II) ions on Papaya leaves (PL) and Petai peels (PP). Experimental condition: Initial concentration = 30 mg/L (PL) and 50 mg/L (PP), biosorbent dose = 0.1 g, contact time = 15 min and strring speed = 200 rpm**

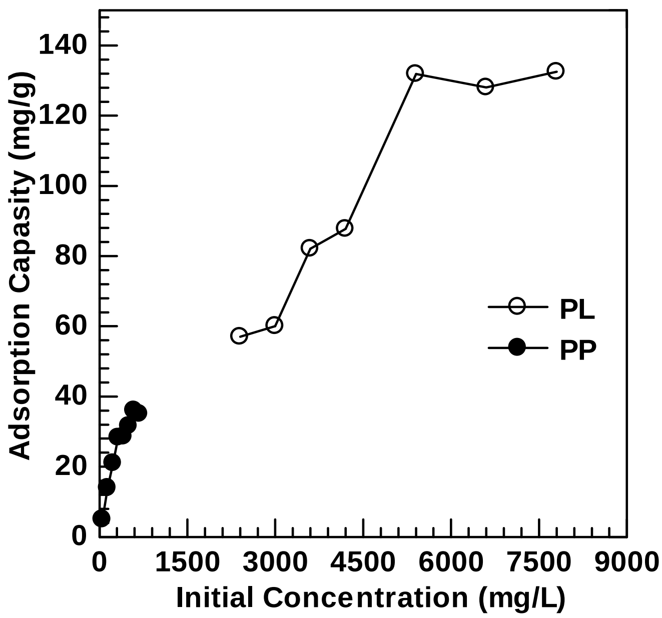


**Fig. 2. Effect of intial concentration on the adsorption capasity of Pb(II) ions on Papaya leaves (PL) and Petai peels (PP). Experimental condition: pH of solution = 4 (PL) and 5 (PP), biosorbent dose = 0.1 g, contact time = 15 min and stirring speed = 200 rpm**

**Effect of Biosorbent Dosage**

Adsorption capacity of Pb(II) ions decreases with increasing mass of biosorbent. Fig. 4 shows biosorbent mass effect on metal ions adsorption.The maximum adsorption of Pb(II) ions using both biosorbent with amount of biosorbent was used 0.1 g. Decreasing adsorption capacity by the increased of biosorbent mass due to unsaturation of active site during the process of adsorption of the Pb(II) ions at a constant concentration and constant volume so biosorbent forming clod due to reducing of surface area [9,12].

**Adsorption Isotherm**

Adsorption isotherms showing the relationship between the amount of adsorbate adsorb by adsorbent and adsorbate concentration in the residual solution. Data of equilibrium adsorption of Pb(II) ions by Papaya leaves and Petai peels were analyzed by Langmuir and Freundlich isotherm.

Langmuir isotherm is determined by the equation:

$$q_e = \frac{Q_m K_L C_e}{1+ K_L C_e} \quad (2)$$

Freundlich isotherm is determined by the equation (3):

$$q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Where "Qe" (mg/g), is the amount of metal ions adsorbed per unit sorbent; "Qm" (mg/g), is the maximum adsorption capacity; "$K_L$" (L/mg), is Langmuir constants; "Ce" (mg/L), is the final concentration of metal ions; "$K_F$" and "n", Freundlich constants. Qm and $K_L$ constants calculated from the slope and intercept by plotting 1/Qe versus 1/Ce (Fig. 5a). Plot of log Qe versus log Ce (Fig. 5b) is used to determine the Freundlich constants, $K_F$ and n.

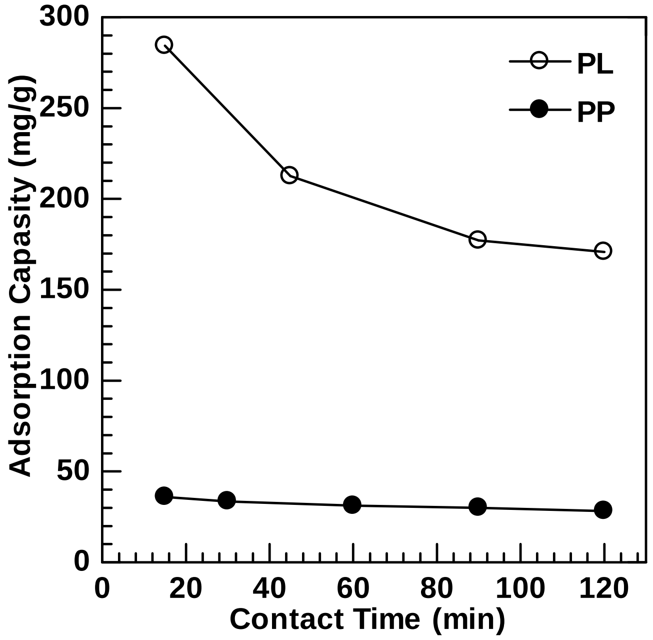


**Fig. 3.Effect of contact time on the adsorption capasity of Pb(II) ions on Papaya leaves (PL) and Petai peels. Experimental condition: pH of solution = 4 (PL) and 5 (PP), Pb(II) ions concentration = 5400 mg/L (PL) and 590 mg/L (PP), biosorbent dose = 0.1 g and stirring speed = 200 rpm**

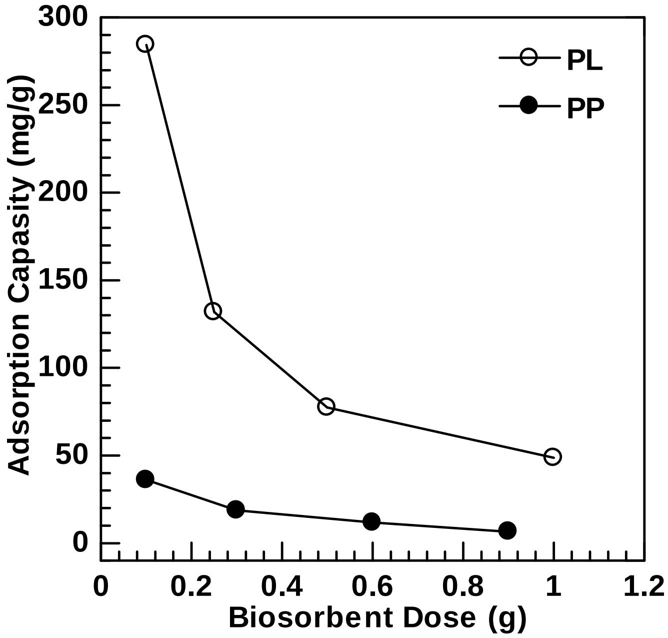


**Fig. 4. Effect of biosorbent dose on the adsorption capasity of Pb(II) ions on Papaya leave (PL) and Petai peels (PP). Experimental condition: pH of solution = 4 (PL) and 5 (PP), Pb(II) ions concentration = 5400 mg/L (PL) and 590 mg/L (PP), contact time = 15 min and stirring speed = 200 rpm**

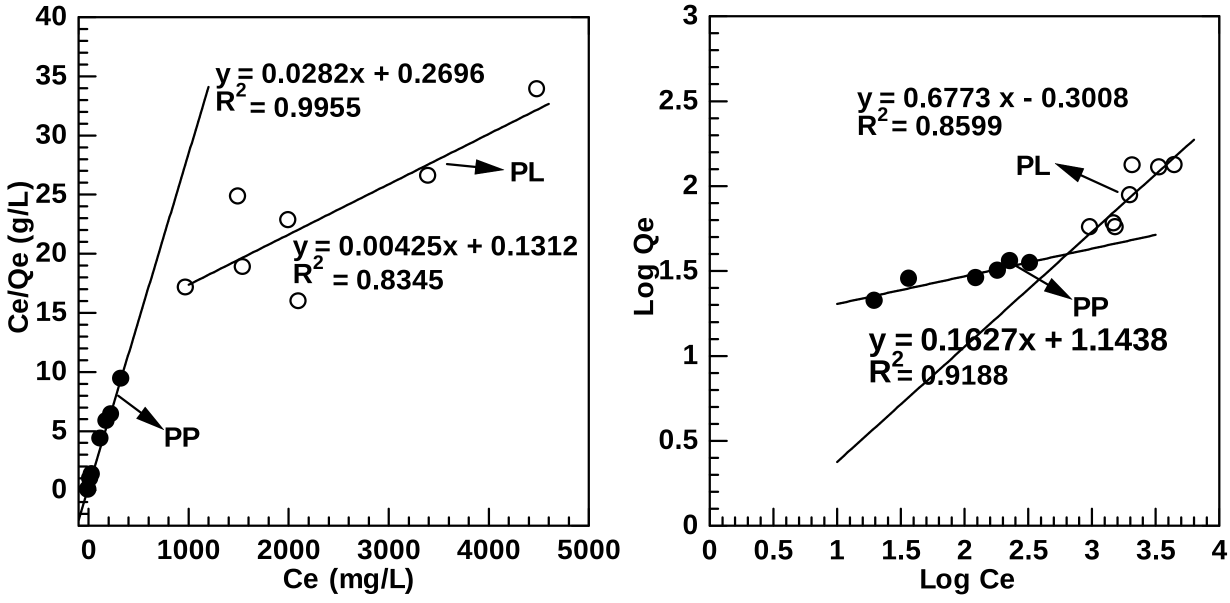


**Fig. 5. Langmuir Isotherm and Freundlich Isotherm for Pb(II) ions biosorption on Pepaya leaves (PL) and Petai peels (PP)**

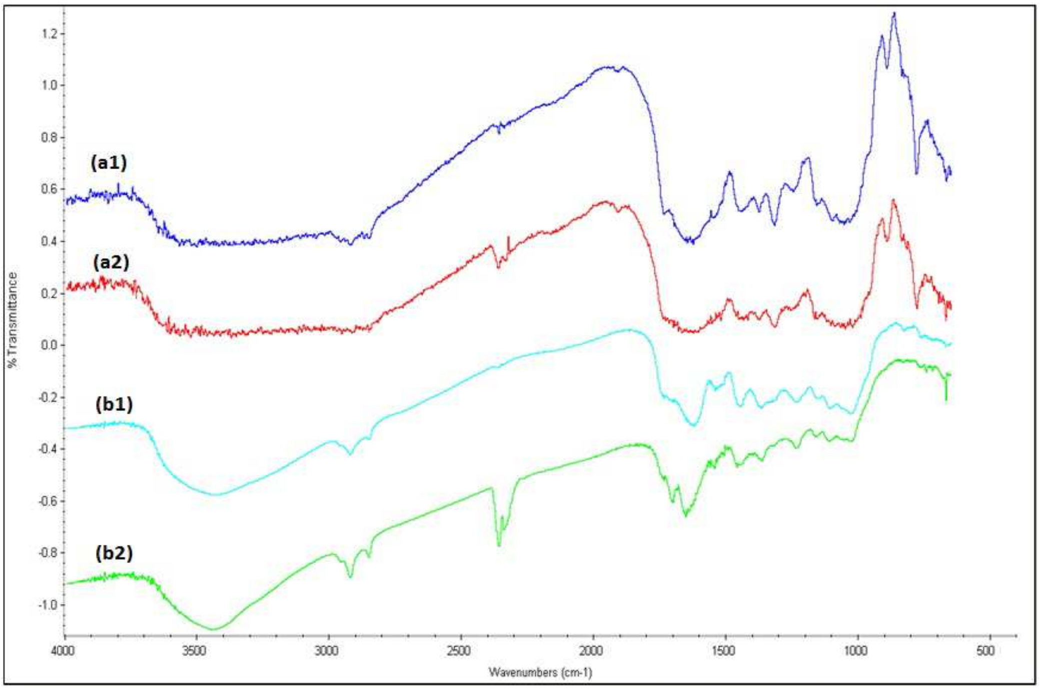


**Fig. 6. FTIR spectrum of Papaya leaves and Petai peels ; (a1) Papaya leaves before biosorption(a2) Papaya leaves after biosorption (b1) Petai peels before biosorption (b2) Petai peels after biosorption**

Fig. 5a and 5b showed Langmuir isotherm and Freundlich isotherm plots at various concentration of Pb(II) ions. In this study, the coefficient correlation ($R^2$) isotherm models shows that this study tended to follow the Langmuir isotherm by using Petai peels This indicates that the adsorption occurs in a monolayer and bound at the active site with chemicals process [1]. While adsorption by using Papaya leaves following Freundlich isotherm. The adsorption occurs in a multilayer and bound at the active site with physical process.

**Fourier Tranform Infra Red (FTIR) Spectroscopy Analysis**

FTIR analysis is used to determine any functional group contained in biosorbent, and to determine which functional groups are active in adsorption of Pb(II) ions in which the spectrum is measured in the range of wave numbers 4000-400 $cm^{-1}$. Broad and strong band with a wavelength of 3500-3200 $cm^{-1}$ indicate the presence of -OH stretch due to hydrogen bonding with polymer compound such as alcohols, phenols and carboxylic. C-H group observed at 3000-2850 $cm^{-1}$ and C=O stretch observed at 1800-1600 $cm^{-1}$. At a wavelength of 1300-1000 $cm^{-1}$, vibration of C-O and alcohol. So we can conclude Papaya leaves and Petai peels containing hydroxyl and carboxyl groups. The functional groups is capable of interacting with metal ions [18].

**Scanning Electron Microscopy (SEM) Analysis**

SEM analysis was performed to see the shape of the surface morphology of Papaya leaves and Petai peels powder with a magnification of 1000x. Fig. 7a is the surface hape before adsorption of metal ions which form a porous surface. While figure 7b is the surface shape after adsorption of metal ions where the pore surface get smaller and indicates metal ions has been adsorbed by both biosorbent.

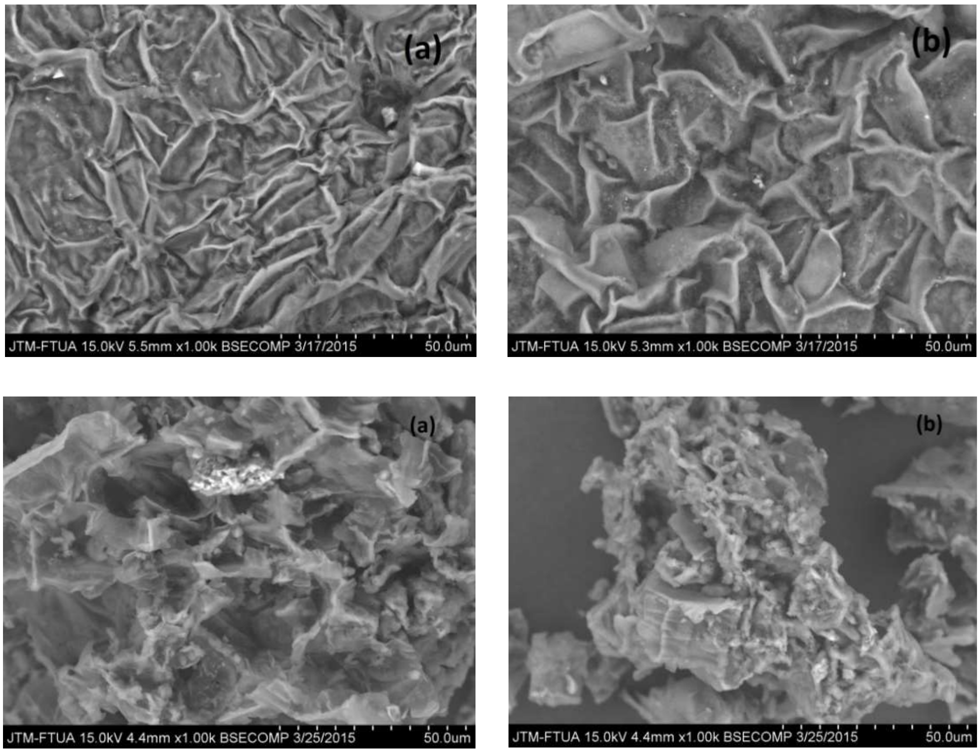


**Fig. 7. Scanning Electron Microscopy of Papaya leaves (above) and Petai peels (below); (a) Before biosorption (b) after biosorption**

## CONCLUSION

Based on this research, it can be conclude that, the Papaya leaves and Petai peels can be used to adsorp Pb(II) ions present in sample in water and can be used to adsorp Pb(II) ions in case of Pb(II) ions present in molecular of animal organ.

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