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# Use Of Pristine Papaya Peel To Remove Pb(II) From Aqueous Solution

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In this study, Carica papaya agro-waste (papaya peel) was employed for Pb(II) uptake from single-solute solutions. The papaya peel-derived (PP) adsorbent namely as raw-PP was employed in sets of batch experiments to evaluate its Pb(II) uptake capacity. To assess the surface characteristics of the adsorbents, the scanning electron microscope (SEM) coupled with energy disperse X-ray (EDX), and Fourier transform infrared spectroscopy (FT-IR) analysis were utilized. The removal amount of Pb(II) using the adsorbent was determined by atomic adsorption spectrometry (AAS). The effects of pH, contact time, initial concentration of Pb(II) and adsorbent dosage were investigated throughout batch processes. The pH value=3 for the Pb(II) adsorption process using the raw-PP was observed as optimum solution pH. The optimum initial concentration of Pb(II) in the solution for raw-PP adsorbent found to be 100 mg/L where the amount of Pb(II) removed was 33.82 mg/g. At the agitating time of 90 min, the adsorption processes using the developed adsorbent reached equilibrium utilizing dosages of 50 mg of raw-PP as an adsorbents. The experimental results obtained using the raw-PP exhibits the high capability and metal affinity of papaya peel waste with removal efficiency percentage of > 85 %. The evaluation results show that the equilibrium adsorption of Pb(II) was best expressed by Freundlich isotherm model ($R^2 > 0.99$). The experimental results confirmed that raw-PP potentially can be employed as low cost adsorbent for Pb(II) uptake from aqueous solutions. The study suggests that future chemical modification of PP may offer increasing of its metal removal capacity.

## 1. Introduction

Heavy metals have many applications in numerous industrial activities referring to their technological importance (Mokaddem et al., 2014). Lead as one the bio-accumulating elements through food chain, is regularly entering to water bodies from discharges of industries such as plating, mining activities, battery manufacture, paint manufacture, etc (Kadirvelu et al., 2001). The application of conventional methods to degrease and remove Pb(II) ion from wastewater is often restricted due to technical and economical constraints. Therefore, the use of various agro-wastes as low cost bioadsorbent was found to be attractive since they are abundantly available and cheap (Hameed, 2009). The papaya fruit received great attention in heavy metal adsorption studies from the various research teams in those countries i.e. Malaysia that have the large papaya cultivation and its agricultural by-products can be employed as potential environmental friendly low-cost adsorbent. According to the literature, papaya agricultural wastes have shown high affinity for different metal ions uptake from aqueous solutions such as cadmium, zinc, lead,

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chromium using its cultivation wastes as a bio-adsorbent (Manjusha et al., 2014). However, the possibility of papaya peel as Pb (II) adsorbent has not been reported and hence is the objective of this paper. In this study, Carica papaya agro-waste (papaya peel (PP)) was employed for Pb(II) uptake from single-solute solutions in sets of batch experiments.

## 2. Methodology

### 2.1 Material

To prepare the synthetic aqueous solution, relative standard stock solutions of Pb(II) (1,000 mg/L) was obtained by dissolution of proper amount of lead nitrate $(PbNO_3)_2$ in distilled water in 1,000 mL volumetric flask and used for further required solution preparation. In this study, all required chemicals were of analytical grade bought from Merck. To adjust the initial pH of stock solution, 0.1 M HCl or 0.1 M NaOH was used. All the adsorption experiments are carried out following batch procedure at room temperature. Smith filter paper and Amicon filter device [Millipore] were used to filter the adsorbent from the solution. Additionally, atomic adsorption spectrophotometer (AAS) (Shimdzu AA-680, Japan) was utilized to determine the Pb(II) uptake concentration of filtrate after each single test.

### 2.2 Adsorbent preparation

The ripened Papaya fruit (Carica Papaya) was collected from the local market, washed carefully with distilled water to remove dirt and then peeled. The washed papaya peel was boiled with distilled water two times for a period of 2 h. The boiled samples are then oven dried for 24 h at 105 $^{o}$C until they became crisp. The dried samples subsequently grinded and sieved using a 45 mesh (355 microns). The papaya peel powder (PP) obtained is stored in an air tight glass container for the future bioadsorption experiments.

### 2.3 Adsorbent surface characterization

To evaluate the morphological characterization of the adsorbent, a scanning electron microscopy (SEM, TM3000, HITACHI, Japan) coupled with energy dispersive X-ray analysis (EDX) were utilized. The surface functional groups, was analysed using Fourier transform infrared spectroscopy (FTIR- NICOLET 5700, Thermo Electron Corporation, Japan). In addition, papaya peel powder analysed by using a BET analyser instrument (Surfer Analyser-SRFA11.0010- Thermo Scientific- Italy) to measure its specific surface area.

### 2.4 Equilibrium study of Pb(II) adsorption

The capability of PP to remove Pb(II) from aqueous solution was investigated through the adsorption batch processes. All uptake experiments were performed in 100-mL flasks containing 20 mL of Pb(II) aqueous solution with a desired concentration at room temperature. The pH adjustment and measurement were made using 0.1 M NaOH and HCl and a pH meter (ORION 2 STAR pH benchtop, Thermo scientific, Italy), respectively. The samples were agitated afterward for a certain period of time under specific stirring conditions (speed of 150 rpm) using an automatic shaker (Systec Laboratory equipment). The Pb(II) uptake study was conducted considering different affecting parameters of contact time (10 to 120 min), absorbent dosage (10 to 200 mg), pH of solution (2 to 11) and initial concentration of Pb(II) ions in the solution (10 to 200 mg/L). The Pb(II) adsorption's isotherms of PP were measured at the different initial Pb(II) concentrations and different time intervals under optimised conditions.

The amount of Pb(II) adsorbed per gram of PP, $q_e$ (mg/g PP) was calculated using mass balance equation (Eq(1)) and the residual Pb(II) ions after adsorption was evaluated by using atomic adsorption spectrophotometer (AAS).

$$q_e = (C_0 - C_e)\ V/W \qquad (1)$$

Where $C_o$ and $C_e$ (mg/L) are liquid phase concentration of Pb(II) at initial and equilibrium, respectively, $V$ (L) is the volume of the solution and W (g) is the dry mass of adsorbent used. The removal efficiency of Pb(II) adsorption process can be measured through Eq(2):

$$\%\ \text{Removal} = [(C_0 - C_e) / C_0] * 100 \qquad (2)$$

## 3. Results and discussion

### 3.1 Characterization of adsorbents

The morphological characterization of raw-PP analyzed by SEM is illustrated in Figure 1 and Table 1 shows the elemental analysis and surface properties of the PP. Based on the SEM images (Figure 1), the porous surface area of PP with high specific surface area (9.63 $m^2/g$) potentially can offer a good uptake opportunity of Pb(II).

The FTIR spectra of pristine PP illustrated in Figure 2, exhibits distinctive broad bands in the frequency range of 3,400 $cm^{-1}$, 1,710 $cm^{-1}$, 1,480 $cm^{-1}$, 1,215 $cm^{-1}$, 1,036 $cm^{-1}$ that indicates the presence of O-H, C=O, C=C/C-C, C-O and C-OH. The variation of peaks in the spectra of PP and PP-Pb loaded and disappearance of some peaks after adsorption could be connected to the ion exchange process that contributes to the interaction between adsorbent surface functional groups and metal ions present in solution during the sorption process (Hossein et al., 2014).

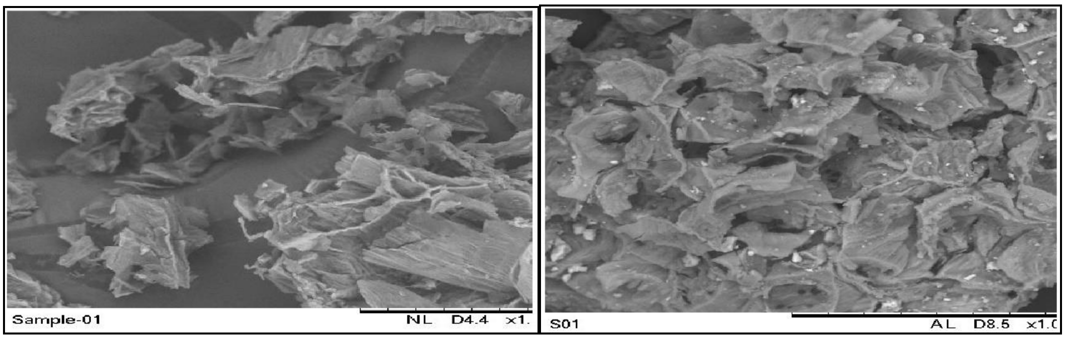

*Figure 1: Pristine papaya peel powder (PP) (a) and PP-Pb(II) loaded.*

*Table 1: Elemental analysis and BET characterization of pristine PP.*

| Name | Carbon % | Nitrogen % | Hydrogen % | Surface area ($m^2/g$) |
|---|---|---|---|---|
| PP-raw | 38.57 | 3.20 | 5.82 | 9.63 |

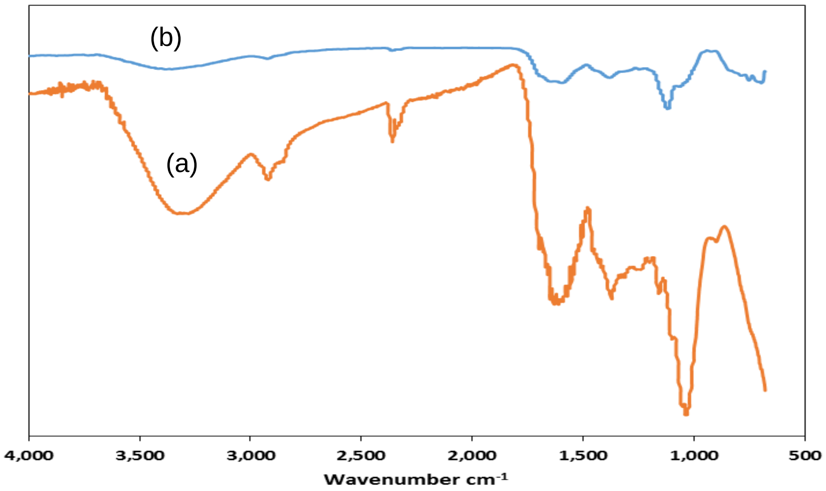

*Figure 2: FTIR spectra of pristine PP (PP-raw)(a) and PP-Pb loaded (b).*

### 3.2 Effect of pH

The pH of solution significantly affects the removal percentage of heavy metal ions as it determines adsorbent surface charge, degree of ionisation and specification of the desired adsorbent. The impact of pH impact is highly dependent on the chemical form of targeting metal ions i.e. pure ionic or hydroxyl-metal form in a specific pH value. Depending on the type of bioadsorbent used, increasing of pH value may substantially increase or decrease the adsorption removal capacity of the process in different optimal pH values (Gardea-Torresdey et al., 2002). Figure 3 shows the effect of pH from 2 to 11, on the Pb(II) uptake capacity of PP. From Figure 3, it appears that the Pb(II) uptake percentage decreased from 36.03

to 33.82 mg/g in line with increase of pH value from 2 to 7 in the presence of constant initial concentration of 50 mg/L Pb(II) ion at equilibrium. The maximum removal percentage of Pb(II) occurred when the pH value reached at 3 (90.30 %, 36.12 mg/g) and then a significant downward trend of adsorption was observed for pH above 5 since Pb(II) ions tend to precipitate in the solution with higher pH level than 6 (basic environment). On the other hand, lower pH value slows down the removal of Pb(II) as $H^+$ and Pb(II) ions are competing for the appropriate sites on the adsorbent surface. Therefore, at higher pH value, pH>2, the competition weakens and Pb(II) ions are able to replace the $H^+$ bound on adsorbent surface and -binding with available surface functional groups like - OH, -COOH, etc (Lee et al., 1999).

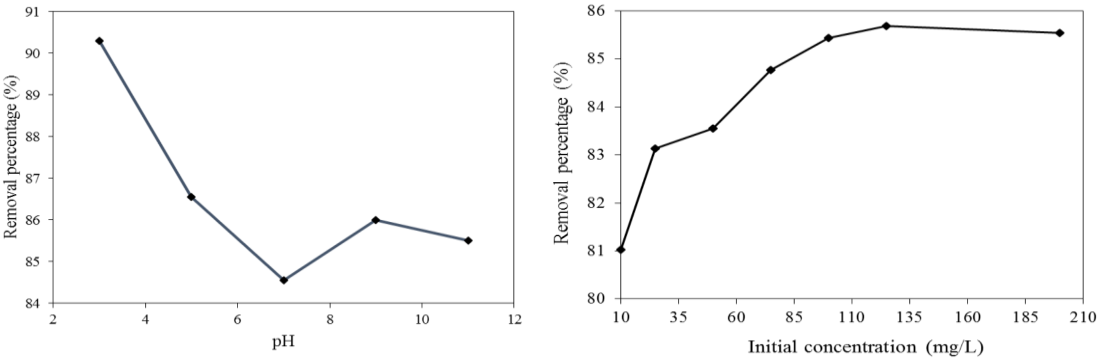

*Figure 3: Variation of Pb(II) removal percentage with solution pH (left) and initial concentration of Pb(II) ion (right).*

### 3.3 Effect of initial concentration of Pb(II) in the solution

The optimum Pb(II) removal in presence of various concentrations of lead ions (10 to 200 mg/L) in the aqueous solution was studied at kinetic equilibrium (90 min, 150 rpm). From Figure 3, it can be clearly observed that the removal amount of Pb(II) from the solution has speeded up in line with the increasing of Pb(II) ions (10 to 100 mg/L) from 3.212 to 33.82 mg/g. The removal percentage was also increased simultaneously from 81 % to 85.43 %. At the initial stages of sorption and in the lower concentration of Pb(II) (lower $C_0$), the ratio of initial mole of metal ions over the available sorption sites was low. Subsequently, the lesser removal percentage of Pb(II) was seen at higher initial concentration of Pb(II) (above 100 mg/L) in the aqueous solution. Such pattern can be predicted as higher amount of adsorbate are competing over limited availability of binding sites on the adsorbent (PP) surface; the fractional sorption become independent of initial concentration and more Pb(II) ions are left unabsorbed in the solution due to saturation of binding sites.

### 3.4 Effect of adsorbent dosage

Figure 4 shows the removal trend of Pb(II) at equilibrium using various PP adsorbent dosage. It was observed that the adsorbent dosage of more than 50 mg with particle size of 355 µ has less metal uptake. Such behaviour indicated that higher adsorbent dosage decreases the metal uptake capacity as the fraction of adsorbent is higher than the existing ions in the aqueous solution. The PP adsorbent dosage beyond 50 mg in 20mL of Pb(II) solution, makes the removal percentage of Pb(II) marginal.

### 3.5 Effect of contact time

The optimum contact time of 90 min is determined after agitating 20 mL of standard aqueous solution containing 100 mg/L of Pb(II) at pH=3 considering various time intervals of 5 to 180 min using 50 mg of PP (see Figure 4). It is observed that the removal percentage increased noticeably at initial stages that can be described by more available surface area and unsaturated sorption sites on adsorbent surface. As process continues during contact time, more Pb(II) ions are adsorbed onto the surface of PP and the number of available sites declines. Usually, the metal ions create a layer with one molecule thickness on the surface of adsorbent. As a result, the sorption capacity of adsorbent relatively decreases since its surface is exhausted gradually. Based on the results, the maximum (85.43 %) removal of Pb(II) by PP was obtained after 90 minutes and the removal trend became constant and insignificant after 90 min.

### 3.6 Adsorption isotherms

To characterize the single metal biosorption process pattern and analyze the obtained results, the equilibrium data were correlated with two well-established isotherm models of Langmuir and Freundlich.

The Langmuir isotherm model defines a monolayer adsorption pattern with consideration of constant adsorption energy whereas the Freundlich model deals with heterogeneous adsorption process. The liner form of the Langmuir (Aman et al., 2008) and Freundlich (El-Ashtoukhy et al., 2008) isotherms are represented as following equations - Eq(3) and Eq(4):

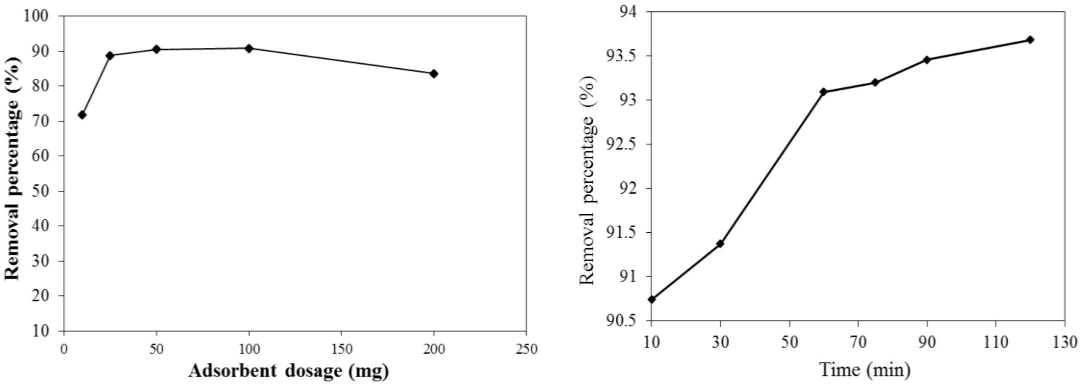

*Figure 4: Variation of removal percentage of Pb(II) with adsorbent dosage (left) and time (right).*

$$C_e/q_e = 1/q_m k_1 + C_e/q_m \qquad (3)$$

where $q_e$ and $C_e$ (mg/L) are the amount of solute adsorbed per unit weight of adsorbent and equilibrium concentration of solute in bulk solution. $q_m$ (mg/g) is the maximum monolayer adsorption capacity and $k_1$ (L/mg) is a constant related to the free energy of adsorption. The Langmuir constant $k_1$ and $q_m$ were calculated from the slope and intercept of the plot from the result of isotherm experiments.

$$\log q_e = \log k_f + (1/n) \log C_e \qquad (4)$$

where $k_f$ (mg/g(L/mg)$^{1/n}$) is the Freundlich constant representing adsorption capacity (bond strength), 1/n is the empirical factor representing the favourability of adsorption and 'n' constant represents the bond energies metal ion where values n > 1 indicate favourable adsorption conditions. $k_f$ and 1/n were calculated from the slope and intercept of the graph of log $q_e$ vs. log $C_e$, respectively (Tong et al, 2011).
The equilibrium results obtained from experiments were well-fitted with Freundlich isotherm model describing by the high coefficient of determination value of $R^2$ = 0.9916. Therefore, it confirms the adsorption of Pb(II) on the heterogeneous surface of PP.

*Table 2: Comparisons of Pb(II) removal capacity using different bioadsorbents.*

| Adsorbent | Pb(II) removal (mg/g) | Reference |
|---|---|---|
| Sugar cane Baggase | 7.30 | Lara et al. (2010) |
| Bagasse fly ash | 2.50 | Gupta and Ali (2004) |
| Olive tree pruning waste | 22.79 | Blazqez et al. (2011) |
| Lalang leaf powder | 13.50 | Hanafiah et al. (2006) |
| Carica papaya leaf powder | 11.30 | Rama Raju et al.(2012) |
| Cow bone | 50.1 | Cechinel et al. (2014) |
| Papaya peel (PP) | 33.82 | This study |

## 4. Conclusion

This study has investigated the adsorption efficiency of Pb(II) using papaya peel powder (PP) bioadsorbent. At pH=3, 50 mg of PP removed 85.43 % of Pb(II) from 20 mL of 100 mg/L Pb(II) solution in 90 min. Based on the comparison of the Pb(II) removal percentages using different types of bioadsorbents derived from alternative materials shows that the methodology used in this study is satisfactory and the value obtained from the experimental results is comparable with those plant-originated waste reported in the literature (see Table 2). This research proves the capability of PP as an efficient alternative for design of an environmental friendly yet economic wastewater treatment process allowing its subsequent usage. Chemical modification of the PP will be followed by the authors in separate studies as it could potentially enhanced the uptake capacity of pristine PP by introducing more functional group on its surface.

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## References

Aman T., Kazi A.A., Sabri M.U., Banoa Q., 2008, Potato peels as solid waste for the removal of heavy metal copper(II) from wastewater/ industrial effluent. Collides surfaces Biointerface. 63, 116-121.

Blazqez G., Martin-Lara M.A., Tenorio G., Calero M., 2011, Batch biosorption of lead from aqueous solutions by olive trees pruning waste: equilibrium, kinetics and thermodynamic study. J. Chem. Eng. 44, 1925-1936.

Cechinel M.A.P., Ulson de Souza S.A.M., Ulson de Souza A.A., 2014, Study of lead(II) adsorption onto activated carbon oroginatinf from cow bone. Journal of Cleaner Production 66, 342-349.

El-Ashtoukhy E.S.Z., Amin N.K., Abdelwahab O., 2008, Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. Desalination, 223, 167-173.

Gardea-Torresdey J.L., Hejazi M., Tiemann K.J., Parsons J.G., Duarte-Gardea M., Henning J., 2002, Use of Hop (Humulus Lupulus) agricultural by-products for the reduction of aqueous lead(II) environmental health hazards. J. Hazard. Mater. 91, 95-112.

Gupta V.K., Ali I., 2004, Removal of lead and chromium from wastewater using bagasse fly ash- a sugar industry waste. J. Colloid Interface Sci. 271, 321-328.

Hameed B.H., 2009, Evaluation of papaya seeds as a novel non-conventional low cost adsorbent for removal of methylene blue. J. Hazard. Mater. 162, 939-944.

Hanafiah M.A.K., Ibrahim S.C., Yahya M.Z.A., 2006, Equilibrium adsorption study of lead ions onto sodium hydroxide modified Lalang (Imperata Cylindrica) leaf powder. J. Appl. Sci. Res. 2, 1169-1174.

Hossain M.A., Ngo H.H., Guo W.S., Ngheim L.D., Hai F.I., Vigneswaran S., Nguyen T.V. 2014, Competitive adsorption of metals on cabbage waste from multi-metal solutions. Bioresour. Technol. 160, 79-88.

Kadirvelu K., Namasivayam C., and Thamaraiselve K., 2001, Removal of heavy metal from industrial wastewater by adsorption on to activated carbon prepared from an agricultural solid waste. Bioresour. Technol. 76, 63-65.

Lara M.A.M., Rico I.L.R., Vicete G.B., Garcia G.B., Hoces M.C., 2010, Modification of sportive characteristics of Sugarcane bagasse for removing lead from aqueous solutions. Desalination. 256, 58-63.

Lee S.H., Shon J.S., Chung H.S., Lee M.Y., Yang J.W., 1999, Effect of chemical modification of carboxyl groups in appl residue on metal ion binding. Korean Journal of Chemical Engineering, 16, 576-580.

Manjusha A., Gandhi N., and Sirisha D., 2014, Removal of chromium (VI) from paint manufacturing industry. International Journal of Research IN Pharmacy and Chemistry, 4(1), 168-180.

Mokaddem H., Azouaou N., Kaci Y., Sadaoui Z., 2014, Study of lead adsorption from aqueous solutions on Agar beads with EPS produced from paenibacillus polymyaxa. Chemical Engineering Transactions. 38, 31-36.

Rama Raju D.S.S., Rao V.N., Prasad P.R., and Babu N.C., 2012, Sorption of lead (II) ions from wastewater using carica papaya leaf powder. International Journal of Engineering & Advanced technology, 2(6), 1577-1581.

Tong K.S., Jain Kassim M., Azraa A., 2011, Adsorption of copper ion from its aqueous solution by novel bioadsorbent Uncaria gambir: Equilibrium, kinetics, and thermodynamic studies. J. Chem. Eng. 170, 145-153.