

# SORPTION OF LEAD (II) IONS FROM WASTEWATER USING CARICA PAPAYA LEAF POWDER

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## Abstract:

*Carica papaya leaf powder as the low-cost adsorbent was investigated as a replacement for cost effective methods of removing lead (II) ions from aqueous solutions. Batch adsorption studies were conducted to examine the effects of pH, agitation time, adsorbent size, adsorbent dosage and initial concentration on the adsorption of Pb (II) by papaya leaf powder. Equilibrium data were fitted in the Langmuir and Freundlich isotherms, and the adsorption kinetics data were evaluated by the pseudo-first-order and second-order kinetic models. The optimum dosage of 1.5gm of carica papaya leaf powder of 52 $\mu$ m size was obtained to remove 89.8% of 100 mg/l concentration of Pb(II) from 50ml of aqueous solution in 1hour respectively. The effective pH for Pb(II) removal is 4. Adsorption isotherm analysis data fitted well to the Freundlich model with a maximum adsorption capacity of 11.13 mg/g. The kinetic experimental data correlated well with the pseudo-second-order kinetic model, which indicated that chemisorption processes could be the rate-limiting step in the adsorption process. The results demonstrated that carica papaya leaf has potential to be employed as the adsorbent for the removal of Pb(II) from aqueous solutions.*

**Keywords:** Adsorption isotherm, Agitation time, Carica papaya leaf, Lead, Kinetics.

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## I. INTRODUCTION

The removal of heavy metals from sewage and industrial waste water is of great interest in the field of water pollution, which is a serious cause of water degradation [1,2,3]. Pollution by heavy metal ions become a major issue worldwide due to their possible toxic effects [4]. Exposure to Lead (Pb) for instance, is widely recognized as a major risk factor for several human diseases, and the structure of industrial ecological systems have made exposure to Pb unavoidable for most people alive today[5,6,7]. Pb (II) ion is also known to bio-accumulate through the food chain often associated with heavy metals such as Zn (II), Cu (II), Cd (II), Mn (II) and Hg (II) that are released into the aqueous environment through variety of sources such as metal smelters, effluents from plastics, textiles, microelectronics and wood preservative producing industries and usage of fertilizer and pesticides[8,9]. These metal ions are stable and are known to be persistent environmental contaminants since they cannot be degraded or destroyed. They are harmful to aquatic life and water contaminated by them remains a serious public health problem to human health [10,11]. It is therefore becomes imperative to determine these metal ion concentrations in bodies of water. Environmental concerns have motivated many physico-chemical methods for heavy metal removal

from aqueous solution. These methods include liquid-liquid extraction (LLE), co-precipitation, resin chelation, electrochemical deposition, ion exchange, coagulation or flocculation and solid -phase extraction (SPE)[12,13]. These techniques however, have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products [14,15]. A number of adsorbents such as activated carbon [16], sargassum [17], chitosan [18], metal oxide gel [19], saw dust [20] have been used for lead (II) removal. Various agricultural products and by-products for the removal of heavy metal from solution has been investigated by Low, K. S., Lee, C. K., & Liew, S. C. [21]. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly. Adsorption, on the other hand, has emerged as a potential alternative to conventional physiochemical technologies in waste-treatment. Adsorption is an effective separation process that has advantages in terms of cost, flexibility and simplicity of design, and ease of operation compared to other techniques. Adsorption also does not result in the formation of harmful substances.

In the present study, papaya leaf has been used as a new low-cost adsorbent to adsorb lead from water. The major characteristic of papaya leaf that is useful in metal removal is due to its chemical composition. As described by [22], papaya leaf is composed of lignin and cellulose as major constituents and may also contain other polar functional groups of lignin, which include alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have ability to some extent to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution.

The present study aimed to investigate the efficiency of papaya leaves as adsorbents for the adsorption of Pb(II) from water. Experiments were conducted to investigate the effects of pH, agitation time, adsorbent size, adsorbent dosage, initial concentration of Pb(II) on the adsorption efficiency of Pb(II) by papaya leaves. Adsorption equilibrium and kinetics had been studied under the optimum adsorption conditions. The Langmuir and Freundlich isotherms were applied to evaluate the adsorption properties in the batch experiments. In addition, the pseudo-first-order and pseudo-second-order kinetic models were also applied to examine the kinetics of the adsorption process.

## II. MATERIALS AND METHODS:

### A. Materials:

Lead Nitrate ( $\text{PbNO}_3$ )<sub>2</sub> was used for the preparation of standard stock solutions of Pb(II) in distilled water. All chemical used in the present study were of analytical grade from Merck. The pH of stock solutions was adjusted using 0.1 M HCl or 0.1M NaOH. The adsorbent was filtered using Whatman filter paper. Atomic absorption Spectrophotometer (Perkin Elmer AA 110Model) was used to measure the Pb(II) concentration.

### B. Preparation of Adsorbent:

The carica papaya leaves were collected from farm lands and washed with water 2-3 times to remove dust and water soluble impurities. The leaves were dried until they became crisp. The dried leaves were powdered and washed two times with distilled water so that the washings were free of colour and turbidity. The resulting powder was dried and sieved to different fractions using rotap sieve shaker. The size fractions were preserved in airtight containers for use as an adsorbent.

### C. Simulated wastewater preparation:

Simulated wastewater sample containing Pb (II) ions was prepared from ( $\text{PbNO}_3$ )<sub>2</sub>. 1000 mg/L stock solution was

prepared. Other concentrations (20 to 140mg/L) were obtained from this stock solution by dilution. Fresh dilutions were used for each experiment. The pH of the simulated wastewater was adjusted to a pH of 4 to prevent hydrolysis. The concentration of metal ions in simulated wastewater was analyzed by Atomic Absorption Spectrophotometer.

### D. Equilibrium Studies of Pb(II) Adsorption:

A series of solutions containing different initial concentrations of Pb(II) ions (in the range of 20 – 140 mg/L) was prepared and employed for the batch adsorption studies at 30°C to check the applicability of the Langmuir and Freundlich adsorption isotherms under optimum conditions obtained previously. The remaining concentration of Pb(II) after adsorption was measured using AAS and the amount of adsorption at equilibrium,  $q_e$  (mg/g) was calculated by:

$$q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  (mg/L) are the liquid-phase concentration of lead at initial and equilibrium, respectively,  $V$  (L) is the volume of the solution and  $W$  (g) is the mass of dry adsorbent used. The adsorption efficiency of Pb(II) can be calculated as:

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \dots\dots\dots (2)$$

### E. Kinetics Studies of Pb(II) Adsorption:

The kinetics studies of Pb(II) adsorption were carried out by batch adsorption at optimum condition. The samples were taken at preset time intervals up to 240 min under temperature of 30°C. The remaining concentration of Pb(II) after adsorption was measured using AAS and the amount of adsorption at time  $t$ ,  $q_t$  (mg/g) was calculated by:

$$q_t = (C_0 - C_t) \frac{V}{W} \quad \dots\dots\dots (3)$$

where  $C_t$  (mg/L) is the liquid-phase concentrations of Pb(II) solutions at any time,  $t$ .

## III. RESULTS AND DISCUSSION

### A. Effect of pH of the aqueous solution:

The pH of the solution has a significant impact on the removal of heavy metals, since it determines the surface charge of the

adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the biosorption of lead (II) ions, the batch equilibrium studies at different pH values were carried out in the range of 1–14 respectively. Fig. 1 shows that the maximum percent removal of lead (II) ions on the adsorbents was observed at pH 3–4 and significantly decreased by reducing the pH values. A significant increase in percentage removal of Pb (II) was obtained as pH value increases from 3 to 4. Downward trend of the % adsorption is noted with an increase in pH above 4. Low pH depresses adsorption of Pb (II), which is due to competition of Pb (II) with H<sup>+</sup> ions for appropriate sites on the adsorbent surfaces. However, with increasing pH, this competition weakens and Pb (II) ions replace H<sup>+</sup> bound to the adsorbent for forming part of the surface functional groups such as –OH, -COOH etc.

#### B. Effect of agitation time on Pb(II) Adsorption:

The optimum agitation time is determined by agitating 50mL of aqueous solution containing 100 mg/L of Pb (II) with varying adsorbent dosages ranging from 0.5 g to 1.5 g and with different adsorbent sizes in the interaction time intervals of 5 min to 4 hr is shown in Fig 2. The optimum time for Pb (II) adsorption is found to be 1 hr from analysis. For a typical experiment with 50 ml of aqueous solution (containing 100mg/l of Pb (II)) with adsorbent dosage of 1.5 g of size 52 $\mu$ m, the % removal increased from 88.91% to 90.52%. It is noticed that the rate of percentage removal is higher in the initial stages because adequate surface area of the adsorbent is available for the adsorption of lead. As time increases, more amount of lead gets adsorbed onto the surface of the adsorbent and surface area available decreases. Normally, the adsorbate forms a thin layer over the surface, which is only one molecule thick. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted. The maximum % removal is attained after 1 hr of agitation. The rate of % removal of lead becomes almost constant and insignificant after 1 hr.

#### C. Effect of adsorbent size on Pb(II) Adsorption:

The results for adsorptive removal of Pb (II) with respect to adsorbent sizes are shown in Fig.3. The percentage removal of Pb (II) is increased with decreasing size of the adsorbent. For an adsorbent dosage of 1.5g, 100mg/L of Pb (II) concentration and 50mL of aqueous solution, the metal % removal increases from 86.87% to 89.89% as the size decreases from 200  $\mu$ m to 52  $\mu$ m. Similar trends are observed with varying dosages of adsorbent ranging from 0.5g to 1.5g. This phenomenon is expected since as the size of the biosorbent decreases, surface area of the particle increases, thereby the number of active

sites on the adsorbent is better exposed to the adsorbate. Hence, the metal uptake would be increased.

#### D. Effect of adsorbent dosage on Pb(II) Adsorption:

Fig.4 represents the effect of adsorption dosage on the percentage removal of Pb (II) at optimum agitation time for different adsorbent sizes 52 $\mu$ m, 100 $\mu$ m and 200  $\mu$ m. It is observed that the metal % removal is increased from 86.87% to 89.89% for adsorbent size of 52 $\mu$ m as dosage is increased from 0.5g to 1.5g. It is evident from the results that the fraction of the metal removed from the aqueous phase increases with an increase in the adsorbent amount. Such behavior is obvious since the metal uptake capacity of the adsorbent increases as its dosage is increased. This is because of the number of active sites available for metal uptake would be more as the amount of the adsorbent increases.

#### E. Effect of initial metal ion concentration:

The effect of initial concentration of Pb (II) in the aqueous solution on the percentage removal of Pb (II) at equilibrium is shown in Fig.5. At an optimum agitation time of 1 hr, the percentage removal of Pb (II) from the aqueous solution is decreased from 91.89% to 86.3% by varying Pb (II) concentrations in the aqueous solution from 20mg/L to 140mg/L. It is noticed from the figure that at lower concentrations, metals are adsorbed by specific sites, while increasing metal concentrations the specific sites are saturated and exchange sites are filled. It is clear that with increasing initial concentrations, the percentage removal decreases.

#### F. Adsorption Isotherm:

The equilibrium study is important for an adsorption process as it shows the capacity of the adsorbent and describes the adsorption isotherm to express the surface properties and affinity of the adsorbent. In the present study, the equilibrium data for Pb(II) adsorption on papaya leaves were evaluated by the Langmuir and Freundlich models.

The Langmuir isotherm is based on assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface [23]. In contrast, the Freundlich isotherm can be used for non-ideal adsorption that involves heterogeneous adsorption [24]. The linearized equations for the Langmuir and Freundlich isotherms are expressed as (4) and (5), respectively.

$$\frac{c_e}{q_e} = \left( \frac{1}{k_a q_m} \right) + \frac{c_e}{q_m} \dots\dots (4)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots (5)$$

A linear graph of (Ce/qe) against (Ce) for papaya leaf adsorbent was plotted. The Langmuir constants qm and ka were determined from the slope and intercept of the plot and tabulated in Table 1. The constant qm (mg/g) is a measure of maximum adsorption capacity of the adsorbent under the experimental conditions and ka (L/mg) is a constant related to the energy of adsorption.

For the analysis of Freundlich isotherm, a linear graph of log(qe) against log(Ce) was plotted by referring to (5). The Freundlich constants, n and Kf, were determined from the slope and intercept of the plot, respectively. The constant ‘n’ indicates the bond energies between metal ion and the adsorbent, whereas Kf (mg/L) is related to bond strength [25]. Results shows that the experimental data was better described by the Freundlich isotherm compared to the Langmuir isotherm. The graph plotted from the Freundlich model yielded a straight line with the regression coefficient (R2) of 0.98. In contrast, the Langmuir isotherm model was less precise, with lower R2 value of 0.89. The value of R2 is regarded as a measure of the goodness-of-fit of experimental data on the isotherm models [25]. Thus, the data of Pb(II) adsorption on papaya leaves may be concluded to perfectly fit the Freundlich isotherm model.

**G. Adsorption Kinetics:**

Various models can be used to analyze the kinetics of the adsorption process. The pseudo-first-order of Lagergren and second-order of Ho & McKay kinetic equations are the most widely used for the adsorption of solutes from a liquid solution [26]. The linear form of equations for the pseudo-first-order and second-order kinetic models can be represented by (6) and (7), respectively.

$$\log (q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \dots\dots (6)$$

$$\frac{t}{q_t} = \left( \frac{1}{k_2 q_e^2} \right) + \frac{t}{q_e} \dots\dots (7)$$

A graph of log(qe – qt) versus time, t was plotted based on the pseudo-first-order model. The parameter of k1 (L/min) is the first-order reaction rate equilibrium constant and qe (mg/g) is the amount of metal adsorbed at equilibrium. The pseudo-first-order kinetic model considers that the rate of occupation of adsorption site to be proportional to the number of unoccupied sites.

In contrast, for the pseudo-second-order equation, k2 (g/mg.min) represents the second-order reaction rate constant. By plotting t/qt against t, the constant k2 was determined from the linear curve. A comparison of the reaction rate constants and R2 values estimated from the pseudo-first-order and second-order equations is presented in Table 2.

From Table 2, R2 value for the pseudo-second-order model is higher than the pseudo-first-order model. This shows that the adsorption of lead on papaya leaves is well-fitted to the pseudo-second-order kinetics model compared to the first-order model. Based on the high regression coefficient value, it can be concluded that the pseudo-second-order kinetics model provides a good correlation for the adsorption of lead ions on papaya leaves and it also suggests that the chemisorption process could be the rate-limiting step in the adsorption process.

**CONCLUSION**

The adsorption of lead from aqueous solution using papaya leaf as the low-cost adsorbent was investigated in batch process. The optimum condition of 1.5gm of carica papaya leaf powder of 52µm size and at pH of 4 was obtained to remove 89.8% of 100 mg/l concentration of Pb(II) from 50ml of aqueous solution in 1hour respectively. The Freundlich adsorption isotherm was best fitted to the experimental data with a maximum adsorption capacity of 11.13 mg/g. Adsorption kinetics of Pb(II) adsorption on papaya leaf followed the pseudo-second-order kinetic model where the chemisorption process may be the rate-limiting step in the adsorption process. This study shows that papaya leaf has high potential to be employed as an effective adsorbent in removal of lead ions and would be useful for the design of wastewater treatment techniques for removal of heavy metals.

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