

Adsorption of Lead from Synthetic Solution using Luffa Charcoal

C. Umpuch, N. Bunmanan, U. Kueasing, and P. Kaewsan

Abstract—This work was to study batch biosorption of Pb(II) ions from aqueous solution by Luffa charcoal. The effect of operating parameters such as adsorption contact time, initial pH solution and different initial Pb(II) concentration on the sorption of Pb(II) were investigated. The results showed that the adsorption of Pb(II) ions was initially rapid and the equilibrium time was 10 h. Adsorption kinetics of Pb(II) ions onto Luffa charcoal could be best described by the pseudo-second order model. At pH 5.0 was favorable for the adsorption and removal of Pb(II) ions. Freundlich adsorption isotherm model was better fitted for the adsorption of Pb(II) ions than Langmuir and Timkin isotherms, respectively. The highest monolayer adsorption capacity obtained from Langmuir isotherm model was 51.02 mg/g. This study demonstrated that Luffa charcoal could be used for the removal of Pb(II) ions in water treatment.

Keywords—Lead (II), Luffa charcoal, Biosorption, initial pH solution, contact time, adsorption isotherm.

I. INTRODUCTION

HEAVY metal contamination of water is an important environmental problem that poses a threat to human health. Lead is a priority toxic pollutant in wastewater discharged from industries such as metal mining, melting, planting, batteries, pesticides, oil paint, pigments, and alloys [1], [2]. At certain exposure levels, lead is a poisonous substance to human. It damages nervous system and causes blood and brain disorders. Long-term exposure to lead or its salts can cause nephropathy, and colic-like abdominal pains [3]. Thus, it is very important to remove lead from the effluents before discharge into natural streams. Although many techniques have been developed, most are expensive or difficult to implement. For example, removal of metal ions from solution by adsorption using activated carbon is one of effective technique; however, the activated carbon is costly and unfavorable to treat large volumes of waste streams

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treatments. To obtain cost-efficient processes, low-cost biosorbents based on agricultural waste or plenty biomaterial are used as a promising alternative. The powder of carbonized biomaterial or charcoal such as bamboo charcoal effectively removes metal ions from aqueous solution of their salts [4]. The IR-spectra characterization of charcoal based on bamboo revealed that –OH, C–H bending, C=O stretching vibration and carbonyl functional groups were mainly responsible for Pb (II) biosorption [5].

In addition, the fruit section of Luffa (*Luffa cylindrica*) is a plenty biomass in Thailand. It may be allowed to mature and used as a bath or kitchen sponge after being processed to remove everything but the network of xylem or fibers. The adsorption of metal ions from aqueous solutions by charcoal based on Luffa sponge is not well documented and the potential use of this adsorbent in the removal of lead ions deserves study. Luffa charcoal may provide an alternative option and be used to partly replace the activated carbon.

For the present study, the adsorption characteristics of Pb (II) ions onto Luffa charcoal were investigated under varying experimental conditions, such as contact time, solution pH, and initial concentration.

II. MATERIAL AND METHOD

A. Preparation of Luffa Charcoal

Luffa sponge was purchased from local market in Ubon Ratchathani, Thailand. Luffa sponge was washed by distilled water and dried in sunlight. The material was crushed and sieved to obtained 300-600 μm particle size and dried in oven at 105°C for an hour. The dried material was burnt at 500°C for 1 h. The obtained Luffa charcoal was stored in desiccators.

B. Chemicals

Stock solution of Pb(II) ions with a concentration of 1000 mg/L was prepared by dissolving 1.599 g of $\text{Pb}(\text{NO}_3)_2$ and 10 mL of HNO_3 in distilled water. The desired Pb(II) concentrations were prepared from the stock solution by making fresh dilutions for each sorption experiment.

C. Batch Biosorption Studies

All adsorption experiments were carried out on a mechanical shaker at 200 rpm using 250 mL Erlenmeyer flasks. A series of adsorption experiments were carried out at room temperature (25°C). The first experiment, the effect of contact time and equilibrium time on lead uptake was carried out. 100mL of 20 mg/L lead solution (pH 5.0) and 0.1g of Luffa charcoal was added into the flasks and then shaken

horizontally for contact time ranging from 5 min to 12 h. The second experiment was to investigate the effect of initial pH solution on lead uptake. The initial pH value of 20 mg/L lead solutions about 100 mL were adjusted the initial pH solution to 2.0, 3.0, 4.0, 5.0 and 6.0 with 0.1N NaOH or 0.1N HNO₃ solutions. Then, the Pb(II) solution and 0.1g of Luffa charcoal was added into the flasks and then horizontally shaken for 24 h at 200 rpm. The third experiment was to study the isotherm. 100 mL of Pb(II) solution at different concentrations of 20, 40, 60, 80 and 100 mg/L (pH 5.0) were prepared and then treated as the procedure in the second experiment.

All solution samples were taken with a syringe and filtrated through 0.45 μm filter membrane for analysis. Pb(II) concentrations in samples were analyzed by an AAS-analyzer. The experiments were run triplicate.

D. Calculation of Removal Percentage and Adsorption Capacity

The percent removal of lead (%A), amount adsorbed at time *t* (*q_t*, mg/g), and amount adsorbed at equilibrium (*q_e*, mg/g), were calculated using the following relationships:

$$\% A = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_t = V \times \frac{C_0 - C_t}{m} \quad (2)$$

$$q_e = V \times \frac{C_0 - C_e}{m} \quad (3)$$

where *C₀* and *C_e* are the initial and final concentrations (mg/L) of metal ions in the flasks, respectively *C_t* (mg/L) is the concentrations of metal ions at time *t*. *V* is the volume of the solution (L) and *m* is the mass of Luffa charcoal (mg/L). The average values of triplicate runs were obtained and analyzed.

III. RESULTS AND DISCUSSIONS

A. Effect of contact time

The sorption rate was rapid during the first 10 min; about 40% of total Pb(II) was removed and then the adsorption capacity increased slowly with the contact time before level off at contact time of 10 h as depicted in Fig. 1. It can be attributed to the fact that the initial stage the free adsorption sites are more, and the slow adsorption rate in later stage is due to slower diffusion of solute into the interior of the adsorbent. Maximum adsorption occurred after 10 h and there was almost no adsorption beyond this time. This characteristic is desirable for the treatment of industrial wastewater and for emergency use, e.g. the leakage of contaminated water, metal ions pollution in ground water, water pollution emergency, which need rapid adsorbents.

The relationship between quantities of lead adsorbed on Luffa charcoal: *q_t* (mg adsorbed lead/g charcoal) versus time (min) was constructed to analyze the effect of contact time to the adsorption efficiency. Moreover, the kinetic data were

analyzed by applying pseudo-first-order and pseudo-second-order models in order to gain a better understanding of the adsorption process.

Pseudo-first order kinetic model [6] is the earliest known one describing the adsorption rate based on the adsorption capacity. The pseudo-first-order rate expression is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (4)$$

where *q_e* (mg/g) and *q_t* (mg/g) are the amounts of adsorbed Pb(II) onto the charcoal at equilibrium and time *t*, respectively. The *k₁* is the rate constant of first-order adsorption. The pseudo-first-order equation does not fit well for whole range of contact time and is in generally applicable over the initial 20-30 min of the sorption process.

Pseudo-second-order kinetic model [7] was developed by Ho in 1995. The fitting of experimental data and second-order kinetic expression for the sorption systems of divalent metal ions using Luffa charcoal was obtained in which chemical sorption is the rate-limiting step. It is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where *k₂* is the rate constant of second-order adsorption.

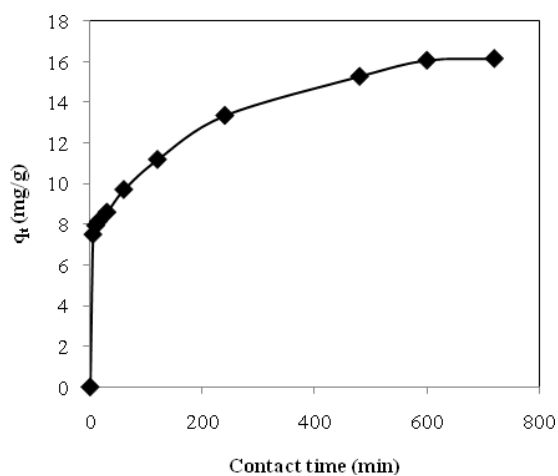


Fig. 1 Effect of contact time on the adsorption of Pb(II) on Luffa charcoal at 20 mg/L initial concentration and pH 5.0 at 25°C

Fig. 2 shows that the data conform to pseudo-second-order model showing that the rate of limiting step is the reaction between the Pb(II) ions and functional groups that can bind metal cations on Luffa charcoal surface.

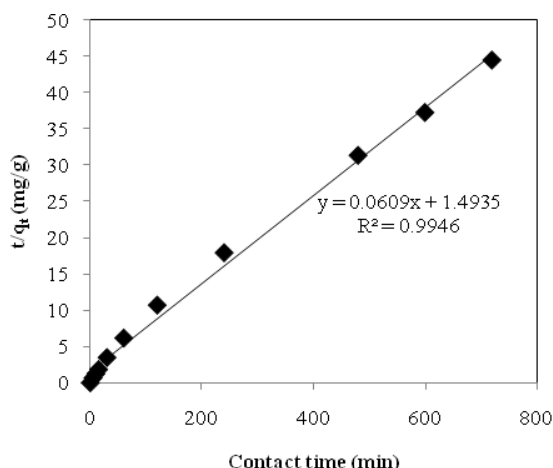


Fig. 2 Pseudo-second-order kinetic model for adsorption of Pb(II) ions on Luffa charcoal.

TABLE I ADSORPTION PARAMETERS OF PSEUDO-FIRST AND PSEUDO-SECOND ORDER MODEL

Kinetic model	Parameter	Value
Pseudo-first-order	k_1 (g/mg.min)	0.0055
	$q_{e,cal}$ (mg/g)	9.84
	R^2	0.8237
Pseudo-second-order	k_2 (g/mg.min)	0.0025
	$q_{e,cal}$ (mg/g)	16.42
	R^2	0.9946

B. Effect of initial pH solution on lead uptake

The lead uptake increases with increasing pH of solution and reaches to maximum value at pH 5.0 as shown in Fig. 3. It was well documented that the pH is a most important parameter that affects the biosorption of heavy metal ions [8], [9].

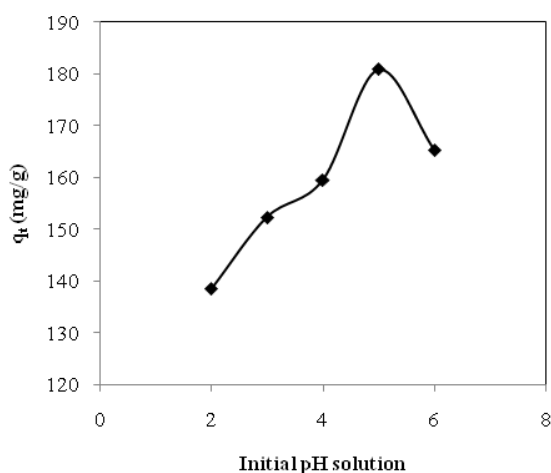


Fig. 3 Effect of pH solution on lead uptake on Luffa charcoal at 20 mg/L initial concentration at 25°C

At low pH, the lead uptake is small because the competitive sorption between proton and metal ions. As the solution pH increases, the number of negatively charge sites increases, which favors the sorption of metal cations. The change in H^+ and OH^- ions in the solution will cause the surface functional groups on charcoal surface to protonate and deprotonate by adsorption of H^+ and OH^- ions. Above the pH value of 6.0, Pb(II) can be precipitated with OH^- ions, and precipitation plays an important role in controlling Pb(II) concentration, so the proportion of heavy metal ions removed from wastewater significantly greater than that in lower pH. It can be concluded that precipitation occurs in general at higher Pb(II) activities while ion exchange predominates at lower Pb(II) activities [10].

C. Adsorption isotherm of lead onto Luffa charcoal

The adsorption isotherm was constructed by plotting equilibrium quantity of Pb(II) adsorbed on Luffa charcoal: q_e (mg adsorbed lead/g adsorbent) versus equilibrium Pb(II) concentration: C_e (mg/L) as shown in Fig. 3. The equilibrium experimental data was fitted to Langmuir's, Freundlich's, and Temkin's equations to analyze adsorption behavior and determine model parameters for Pb(II) as shown in Table 1.

The Langmuir [9] isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. The Langmuir model is based on the assumption of adsorption homogeneity, such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species. If Pb(II) adsorption follows the Langmuir model, the adsorption process can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (6)$$

where C_e (mg/L) is the equilibrium concentration of Pb(II) in solution, q_e (mg/g) the adsorption capacity at equilibrium, q_m (mg/g) the maximum adsorption capacity and b is the Langmuir constant related to the rate of adsorption. The Langmuir equation obeys Henry's law at low concentration.

The Freundlich [9] equation is the empirical relationship whereby it is assumed that the adsorption energy of Pb(II) binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. The Freundlich isotherm model is usually adopted for heterogeneous adsorption [11]. One limitation of the Freundlich model is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. This isotherm can be described as follows:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

where q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the equilibrium concentration of Pb(II) in solution and k_f and n are the physical constants of the Freundlich adsorption isotherm. The k_f and n are indicators of the

adsorption capacity and adsorption intensity, respectively. n is a constant representing the mutual interaction of sorbed species. Experimental values of n are usually greater than unity and this means that the forces between the sorbed molecules are repulsive. In addition, the closer the n value of the Freundlich sorption equations is the zero, the more heterogeneous is the system [12].

The Temkin isotherm [13] equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy. The linear form of Temkin isotherm can be expressed as:

$$q_e = B \log k_t + B \log C_e \quad (8)$$

Where $B = RT/b$ represents heat of adsorption, T is the absolute temperature in Kelvin and R is the universal gas constant, $1/b$ indicates the adsorption potential of the adsorbent while k_t (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. The plot of q_e versus $\log C_e$ enables the determination of isotherm constants k_t and B .

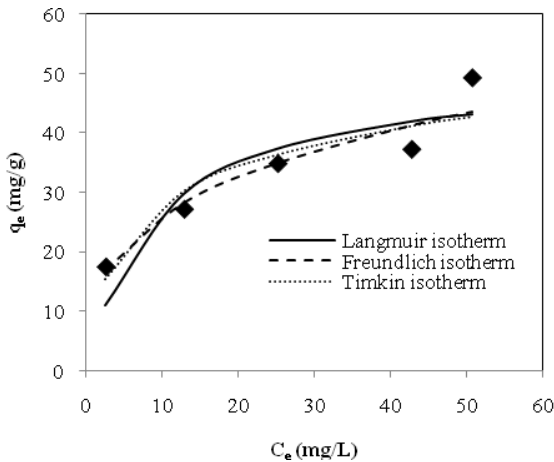


Fig. 4 Adsorption isotherm of Pb(II) onto Luffa charcoal at pH 5 at 25°C

TABLE II ADSORPTION PARAMETERS OF LANGMUIR, FREUNDLICH AND TEMKIN ISOTHERMS

Equilibrium model	Parameter	Value
Langmuir isotherm	q_{max} (mg/g)	51.02
	b (L/mg)	0.11
	R^2	0.9267
Freundlich isotherm	k_f (mg/g)(L/g) ^{1/n}	12.74
	n	3.19
	R^2	0.9535
Temkin isotherm	k_t (L/mg)	2.18
	b (J/mol)	272.56
	B (L/g)	9.0934
	R^2	0.8681

It was found that Freundlich adsorption isotherm model was better fitted for the adsorption of Pb(II) ions than Langmuir and Temkin isotherms, respectively. The highest monolayer adsorption capacity obtained from Langmuir isotherm model was 51.02 mg/g for the adsorption of Pb(II) ions by Luffa charcoal.

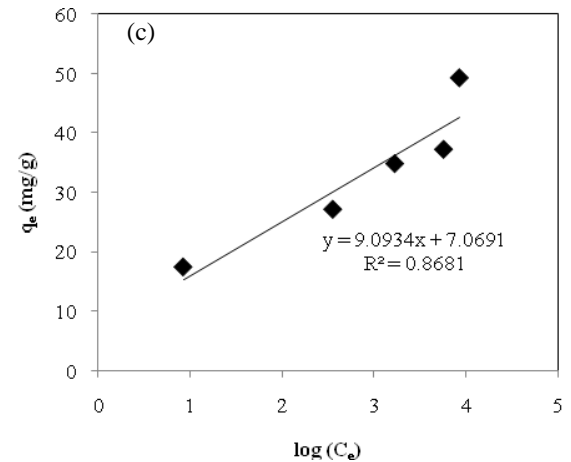
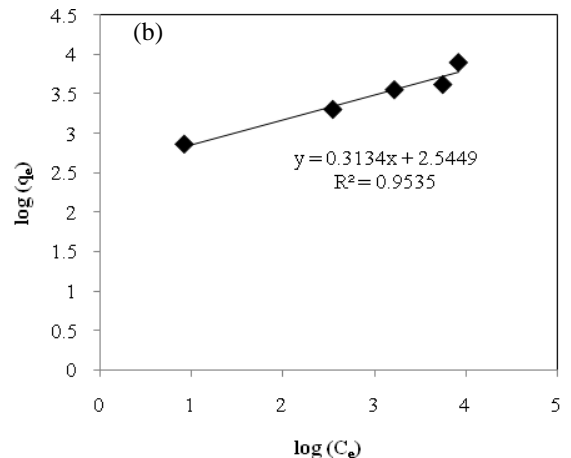
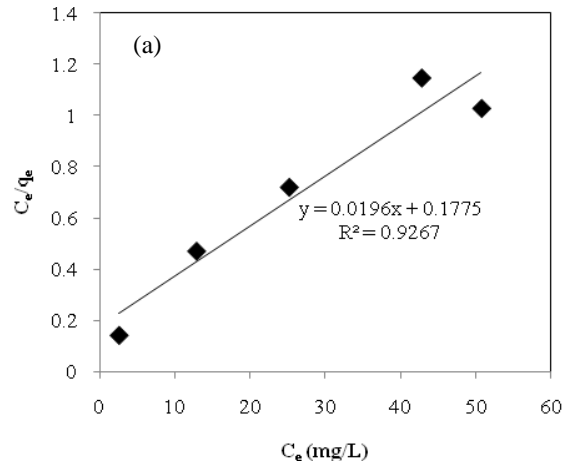


Fig. 5 Langmuir (a), Freundlich (b), and Temkin (c) adsorption isotherms of Pb (II) ions on Luffa charcoal

IV. CONCLUSIONS

In the present study, batch adsorption experiments for the adsorption of Pb(II) ions from aqueous solutions have been carried out using Luffa charcoal as adsorbent. The adsorption characteristics have been examined at different contact time, different initial pH solution values, and different initial Pb(II) ions concentrations. The obtained results can be summarized as follows:

1. The adsorption rate of Pb(II) ions was very fast initially, and about 40% of total Pb(II) was removed within 10 min. Thereafter, the adsorption capacity increased slowly with the contact time before reaching a plateau value after the contact time of 10 h, and then remained constant.
2. Generally, adsorption capacity of Pb(II) ions by Luffa charcoal increased with an increase in the pH of the adsorbate solution. The optimum pH for Pb (II) removal is 5.0.
3. Freundlich adsorption isotherm model was better fitted for the adsorption of Pb(II) ions than Langmuir and Timkin isotherms, respectively. The highest monolayer adsorption capacity obtained from Langmuir isotherm model was 51.02 mg/g for the adsorption of Pb(II) ions by Luffa charcoal.

Studies on batch adsorption indicate that the Luffa charcoal has efficient adsorption capacity for Pb(II) ions and its use may significantly lower the cost of water treatment.

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