

Equilibrium Adsorption Study of Lead Ions onto Sodium Hydroxide Modified Lalang (*Imperata cylindrica*) Leaf Powder

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Abstract: *Imperata cylindrica* (IC) leaf powder was modified by thermal treatment using NaOH solution. Adsorption was carried out in a batch process with different concentrations of lead ions by varying pH, amount of adsorbent, contact time and temperature. Adsorption equilibrium was established in about 20 min. Adsorption of lead was found to increase with increasing amount of adsorbent and pH, but decreased with increasing temperature indicating exothermic nature of adsorption. The kinetic data corresponded well with the pseudo-second-order equation. The optimum pH range for adsorption of lead was 4 – 5. The experimental results were fitted well to the Langmuir isotherm and the maximum adsorption capacity was 13.50 mg g⁻¹. The negative values of the Gibbs free energy (ΔG) indicate spontaneous nature of adsorption process.

Key words: Adsorption; *Imperata cylindrica*; Kinetic, Langmuir isotherm, Lead ion.

INTRODUCTION

The tremendous increase in the amount of lead in aquatic environment has become a major concern by scientists all over the world. Lead is one of the toxic heavy metals widely discharged into the environment as industrial waste in many countries, causing serious soil and water pollution. Lead has been known to pollute the environment by waste streams, which originates from metallurgical industry, electroplating and metal finishing industries, paint manufacture, storage battery manufacture, petroleum refining and drainage from ore mines. According to Bhattacharyya and Gupta^[2], lead can enter or adsorbed into human body through inhalation, skin contact or with diet, resulting in adverse health effects on every system in the body. Excessive exposure to lead may lead to anemia, mental retardation, coma, seizures and bizarre behavior^[3]. Numerous methods have been introduced for removing lead from wastewaters mainly chemical precipitation, chemical oxidation or reduction, ultrafiltration, electrochemical treatment, reverse osmosis, phytoextraction, electrodialysis, application of membrane technology, evaporation recovery, solvent extraction and ion exchange processes. However, the aforementioned techniques are very expensive, may produce large volume of wastes and not economically feasible for small and medium industries^[1,19]. Adsorption processes using natural adsorbents or agricultural waste products are becoming the new alternative for wastewater treatment because they are cheap, simple, sludge free and involve small initial

cost and land investment. Heavy metals adsorption technology by biomass has some major advantages especially its effectiveness in reducing the concentration of heavy metal ions to very low levels and the adsorbent materials itself are inexpensive^[18]. In this work, the effectiveness of adsorption of lead ions by NaOH modified IC leaf powder was studied. IC has been ranked as one of the ten worst weeds of the world^[11]. It is widely distributed in Africa, Asia, Australia and America. This species is considered a pernicious pest plant due its ability to successfully displace desirable vegetation and disrupt ecosystems. This study determines the parameters that influence adsorption of lead such as pH of the solution, temperature, initial lead concentration, contact time and adsorbent dose. The kinetic or rate of adsorption based on pseudo-second-order equation was also studied.

MATERIALS AND METHODS

Preparation of adsorbent: IC leaves were collected from the surrounding area of Universiti Teknologi MARA, Pahang campus, Malaysia. The leaves were allowed to dry at room temperature in a shade for 72 h. The leaves were extensively washed with distilled water to remove dirt, dried in an oven at 80 °C for a period of 24 h, then ground and screened to obtain the average particle size of 355 μm . Then, 20 g of the leaf powder was mixed with 200 mL of NaOH (0.1 M). The mixture was heated at 120 °C for 30 min and occasionally was stirred. The leaf powder was separated by filtration using 0.45 μm membrane filter paper, washed extensively with distilled

water until the washings were free of color and the final pH of effluent reached 7. The drying process was carried out at temperature of 50 °C, overnight in order to avoid thermic deactivation of the adsorbent surface^[15].

Adsorption experiments: The adsorption experiments were performed in a batch process under the following experimental conditions:

Initial Pb ²⁺ concentration (mg L ⁻¹)	5, 20
Adsorbent amount (g L ⁻¹)	4, 20, 40
Contact time (min)	0 – 120
Temperature (°C)	30, 40
pH	2 – 5
Average adsorbent size (µm)	355

All the chemicals used in the experiments were of analytical grade reagents. Pb(NO₃)₂ (Merck) was used as the source of Pb²⁺ and all of the solutions were made in distilled water. The solutions of Pb²⁺ were prepared from a stock solution containing 1000 mg L⁻¹ of Pb²⁺. The kinetic experiments were carried out in a series of Erlenmeyer flasks of 100 mL capacity by agitating a pre-weighed amount of NaOH modified IC leaf powder with 25 mL of the aqueous Pb²⁺ solution in a constant temperature (30°C), water bath shaker (Mettler, Germany) for a pre-determined time interval at a constant speed of 150 rpm. The initial pH of the solution was fixed at 4 by adding drops of 0.1 M HCl or NaOH solutions. For isotherm study, 0.1 g of adsorbent was mixed with 25 mL lead solutions at various concentrations (5 – 100 mg L⁻¹) and the mixtures were shaken for 60 min at temperature of 30 °C. The experiments on the effect of pH, temperature and amount of adsorbent were performed at temperature of 30 °C (unless otherwise stated) by mixing 0.1 g (unless otherwise stated) of NaOH modified IC powder with 25 mL lead solutions (20 mg L⁻¹). After adsorption, the mixture was filtered through Whatman filter paper (No. 40). The concentrations of lead in the solutions before and after equilibrium were determined by atomic absorption spectrophotometer (Perkin Elmer, Analyst 400) using air-acetylene flame. All experiments were performed in duplicates and results are reported as average.

Metal uptake: The amount of Pb²⁺ adsorbed, q_t (mg g⁻¹) was computed by using the following equation:

$$q_t = \frac{C_o - C_t}{m} V \quad (1)$$

where C_o and C_t are Pb²⁺ concentrations in mg L⁻¹ before and after adsorption at time t, V is the volume of adsorbate in liter (L) and m is the weight of the adsorbent in gram (g).

RESULTS AND DISCUSSIONS

Adsorption kinetic: Adsorption kinetic, which describes the adsorbate adsorption rate, is an important characteristic in evaluating the efficiency of adsorption. The adsorption data at two initial Pb²⁺ concentrations is shown in Fig. 1. The plots show that kinetic of adsorption of Pb²⁺ consisted of two phases; an initial rapid phase where adsorption was fast and a second slower phase where equilibrium uptake was achieved. The first phase is related to external surface adsorption and adsorption occurs instantaneously. The second phase is the gradual adsorption stage before the metal uptake reaches equilibrium. The time to reach equilibrium is 20 min and the maximum amounts of Pb²⁺ adsorbed are 1.213 and 4.929 mg g⁻¹ for lead concentrations of 5 and 20 mg L⁻¹, respectively. According to Bhattacharyya and Gupta^[2], the initial high rate of metal uptake may be attributed to the existence of the bare surface. However, the number of available adsorption sites decreased as the number of Pb²⁺ ions adsorbed increases. The enhanced adsorption of metal ion with increase in agitation time may also be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in the kinetic energy of hydrated ions^[12]. By increasing the agitation time, the boundary layer resistance will be reduced and there will be an increase in the mobility of ions in the solution. For the following experiments, the contact time was maintained for 60 min to ensure that equilibrium was really achieved.

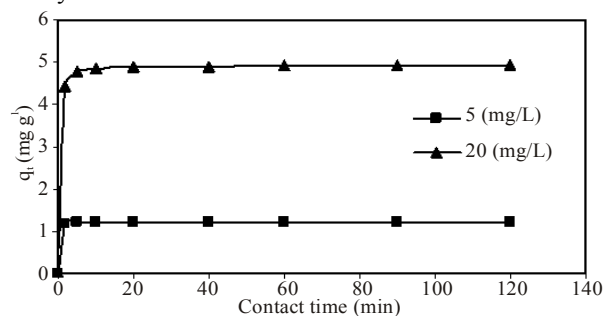


Fig. 1: Effect of initial lead concentration and time on lead adsorption onto NaOH modified IC leaf powder.

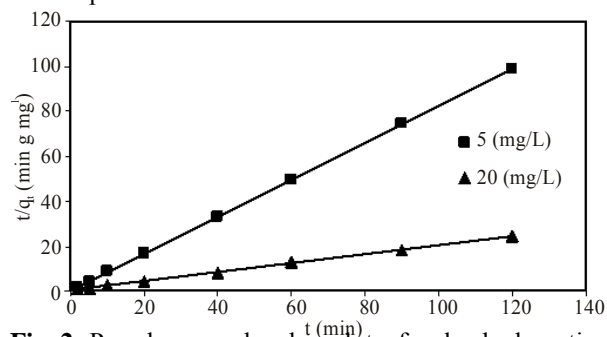


Fig. 2: Pseudo-second-order plots for lead adsorption onto NaOH modified IC leaf powder.

Table 1: Comparison between adsorption rate constants, q_e estimated and coefficients of correlation associated to the pseudo-second-order kinetic model.

[Pb] (mg L ⁻¹)	Pseudo-second-order kinetic model				
	k (g mg ⁻¹ min ⁻¹)	q _e (mg g ⁻¹)	R ²	h (mg g ⁻¹ min ⁻¹)	q _{e,exp} (mg g ⁻¹)
5	59.098	1.213	1.000	86.956	1.213
20	1.143	4.936	1.000	27.855	4.929

Table 2: Amount of lead removed (%) and adsorbed (mg g⁻¹) at three different adsorbent doses

Amount of adsorbent (g)	Removal (%)	Lead adsorbed (mg g ⁻¹)
0.1	98.2	4.93
0.5	97.8	0.98
1.0	98.1	0.49

Table 3: Comparison of ΔG values at two different temperatures for Pb(II) adsorption onto NaOH modified IC leaf powder

[Pb] mg L ⁻¹	T = 30 °C			T = 40 °C		
	q _e (mg g ⁻¹)	K _c	ΔG (kJ mol ⁻¹)	q _e (mg g ⁻¹)	K _c	ΔG (kJ mol ⁻¹)
20	4.936	69.423	- 10.68	4.750	19.080	- 7.67

Identifying the slowest step or rate-determining step is also crucial in any kinetic study. In order to investigate the controlling mechanisms of adsorption processes, the pseudo-second-order^[9] was used to test the experimental data. The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (2)$$

where $h = kq_e^2$ can be regarded as the initial adsorption rate as $t \rightarrow 0$ and k is the rate constant of second-order adsorption (g mg⁻¹ min⁻¹). The plot t/q_t versus t should give a straight line if second-order kinetic is applicable and q_e , k and h can be determined from the slope and intercept of the plot, respectively. The plot of t/q_t versus t for pseudo-second-order model (Fig. 2) yields very good straight lines (correlation coefficient, $R^2 > 0.99$). The pseudo-second-order rate constants were in the range of 1.143 to 5.91×10^1 g mg⁻¹ min⁻¹, as shown in Table 1. The increase in initial adsorption rate (h) with decreasing lead concentration could be caused by the lower probability of collision between lead ions, hence lead ions could be bonded faster to the adsorption sites of the adsorbent^[20]. The theoretical values of q_e also agree very well with the experimental ones. Both facts suggest that the adsorption of Pb²⁺ ions by NaOH modified IC leaf powder follows the pseudo-second-order kinetic model, which relies on the assumption that chemisorption may be the rate-limiting step. This finding was similar to other studies on the adsorption of lead by low-cost adsorbents. For instance, pseudo-second-order kinetic was also observed in the adsorption of cadmium and lead by spent grain^[14] and rubber (*Hevea brasiliensis*) leaf powder^[7,8].

Effect of pH: pH is an important parameter for adsorption process due to its influence on the ionization state of the functional groups on the surface of adsorbent

(carboxylate, hydroxy, etc) and different ionic forms of lead. According to Sekar *et al.*^[16], above pH 5.5, lead starts to precipitate as Pb(OH)₂. Therefore experiments were performed in the pH range 2 – 5. As can be seen in Fig. 3, the adsorption of Pb²⁺ ions from aqueous solution is mainly influenced by solution pH. It is noticed that adsorption increased continuously with the decrease in acidity until it reached maximum adsorption capacity at pH 5. The increase in lead adsorbed as pH increases can be explained on the basis of a decrease in competition between proton (H⁺) and lead ions on the surface of adsorbent. As pH increased, more adsorbent surface would be exposed and carried negative charges, with subsequent attraction of lead ions^[4].

Effect of adsorbent dose: The dependence of adsorption of lead on the amount of NaOH modified IC leaf powder was studied at room temperature (30 °C) at pH 4.0 by varying the amount of adsorbent from 0.10 to 1.0 g while keeping the volume (25 mL) and concentration of the metal solution constant. The result is shown in Fig. 4 and Table 2. The amount of lead adsorbed (mg g⁻¹) was found to decrease with increasing amount of adsorbent. The amount of Pb(II) ions adsorbed decreased from 4.93 to 0.49 for adsorbent amount of 0.10 and 1.0 g, respectively. According to Shukla *et al.*^[17], the decrease in adsorption density with increase in adsorbent amount is due to the high number of unsaturated adsorption sites. Based on Table 2, an amount of 0.1 g of the adsorbent was found to be sufficient to remove 20 mg L⁻¹ lead from the aqueous solution.

Effect of temperature: The effect of temperature on lead adsorption for lead concentration of 20 mg L⁻¹ is shown in Fig. 5 and Table 3. It is found that the amount of lead adsorbed (mg g⁻¹) decreased with increasing temperature, indicating exothermic nature of adsorption. A similar finding was also observed by Han *et al.*^[6] for the

Table 4: Summary of rate constants, initial adsorption rates and amount of lead adsorbed predicted from pseudo-second-order equation at two different temperatures

Temperature (°C)	Pseudo-second-order kinetic model				
	k (g mg ⁻¹ min ⁻¹)	q _e (mg g ⁻¹)	R ²	h (mg g ⁻¹ min ⁻¹)	q _{e,exp} (mg g ⁻¹)
30	1.143	4.936	1.000	27.855	4.929
40	8.059	4.750	1.000	181.82	4.750

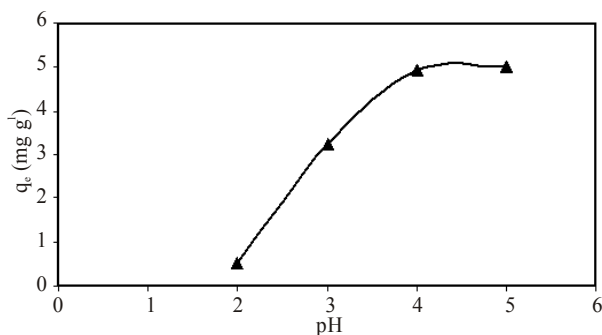


Fig. 3: Effect of pH on lead adsorption onto NaOH modified IC leaf powder.

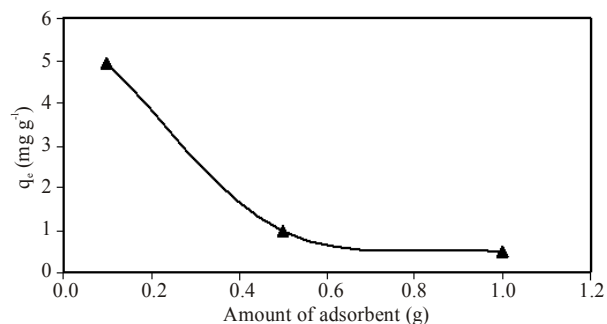


Fig. 4: Effect of adsorbent dose on lead adsorption onto NaOH modified IC leaf powder.

biosorption lead ions by waste beer yeast. At equilibrium, the amount of lead adsorbed were 4.929 and 4.750 mg g⁻¹ at temperatures 30 and 40 °C, respectively. At higher temperature (40 °C), the time taken for adsorption to reach equilibrium was much shorter (5 min). The Gibbs free energy (ΔG) for lead adsorption was calculated using the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \quad (3)$$

$$\Delta G = -RT \ln K_c \quad (4)$$

where K_c is the equilibrium constant (unitless), C_e is the equilibrium concentration in solution (mg L⁻¹) and C_{Ae} is the solid-phase concentration at equilibrium (mg L⁻¹). Spontaneity of the adsorption process was demonstrated by the negative values of ΔG (values varied from - 10.68 kJ mol⁻¹ at 30 °C to - 7.67 kJ mol⁻¹ at 40 °C) as shown in Table 3. The negative values of ΔG indicate that the equilibrium:

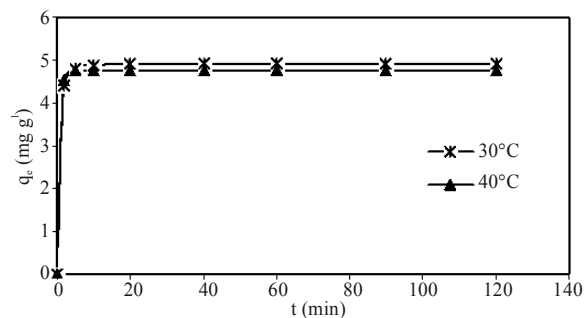


Fig. 5: Effect of temperature on lead adsorption onto NaOH modified IC leaf powder.



shifts to the forward direction in a spontaneous manner leading to binding of Pb²⁺ ions on to surface constituents of NaOH modified IC leaf powder. The pseudo-second-order plot of t/q_t versus t (Fig. 6) yields very good straight lines (correlation coefficient, R² > 0.99). The values of rate constant, initial adsorption rate and amount of lead adsorbed predicted from pseudo-second-order model at two different temperatures are given in Table 4. In order to find the activation energy of the adsorption reaction, the following equation was applied:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (6)$$

where k₂ and k₁ are the pseudo-second-order rate constants at two different temperatures, E_a is the activation energy (kJ mol⁻¹), R is the gas constant 8.314 J mol⁻¹ K⁻¹ and T₂ and T₁ are temperatures in Kelvin. The high value of activation energy (154.1 kJ mol⁻¹) calculated from equation 6 suggests chemisorption process was significant in the adsorption of lead ions onto NaOH modified IC leaf powder^[10].

Adsorption isotherm: The maximum adsorption capacity of NaOH modified IC leaf powder for lead was investigated over a range of lead concentrations. Fig. 7 shows the plot of the adsorption capacity, q_e (mg g⁻¹) versus the equilibrium concentration of lead ions in the solution, C_e (mg L⁻¹). The amount of lead adsorbed was found to increase with increasing lead concentration until the maximum adsorption capacity was achieved. The distribution of metal ions between liquid and solid phases

Table 5: Langmuir adsorption isotherm for removal of Pb²⁺ ions onto NaOH modified IC leaf powder.

Langmuir constants		
Q _{max} (mg g ⁻¹)	b(L mg ⁻¹)	R ²
13.50	1.10	0.9997

Table 6: Separation factor, R_L

Temperature(°C)	Pb(II) concentration (mg L ⁻¹)					
	5	10	20	37.6	58.6	100
30	0.154	0.091	0.043	0.023	0.015	0.010

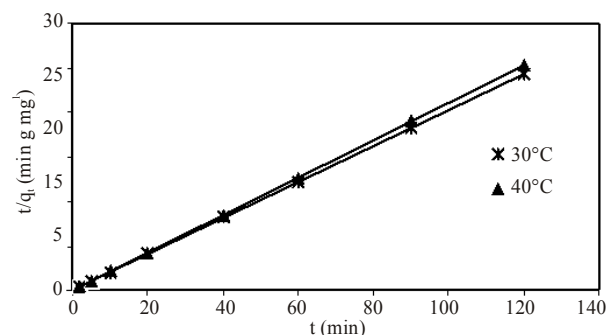


Fig. 6: Pseudo-second-order plots for lead adsorption onto NaOH modified IC leaf powder at two different temperature.

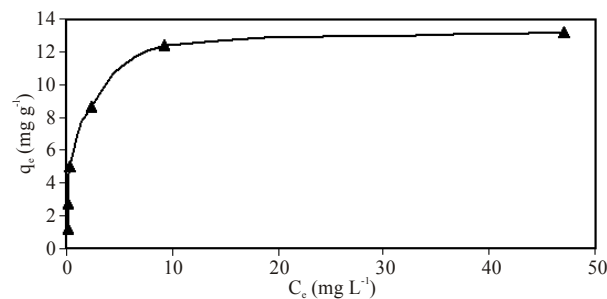


Fig. 7: Adsorption isotherm plot for lead adsorption onto NaOH modified IC leaf powder.

is generally described by using the Langmuir^[13] adsorption isotherm equation. The Langmuir equation assumes uniform energies of adsorption onto the adsorbent surface and no transmigration of adsorbate in the plane of the surface. The Langmuir adsorption isotherm is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}} \quad (7)$$

where, C_e is the equilibrium Pb²⁺ concentration (mg L⁻¹), q_e the amount of Pb²⁺ adsorbed at equilibrium (mg g⁻¹), Q_{max} is the maximum adsorption capacity and b is the isotherm constant related to the affinity of the binding sites. Fig. 8 shows the Langmuir adsorption isotherm obtained by plotting C_e/q_e versus C_e. Based on the R² value obtained from the isotherm model, it is clear that the

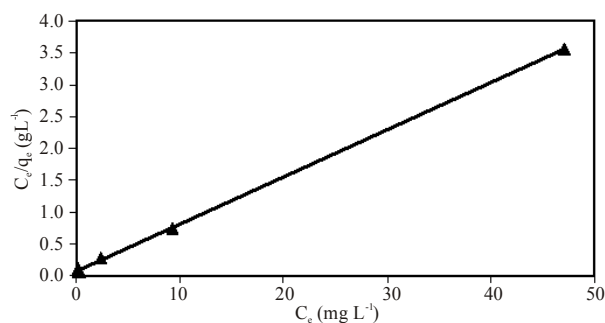


Fig. 8: Langmuir plot for lead adsorption onto NaOH modified IC leaf powder.

Langmuir equation has best fitted for the adsorption of lead onto NaOH modified IC leaf powder. The maximum adsorption capacity determined from the Langmuir equation was found to be 13.50 mg g⁻¹, as shown in Table 5. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L or separation factor, defined as^[5]:

$$R_L = \frac{1}{1 + bC_o} \quad (8)$$

where C_o is the initial lead concentration and b is obtained from the Langmuir plot. For favorable adsorption, 0 < R_L < 1, unfavorable adsorption, R_L > 1 and R_L = 1 represents linear adsorption while the adsorption process is irreversible if R_L = 0. The R_L values at different concentrations, which are listed in Table 6 indicate favorable adsorption of lead onto NaOH modified IC leaf powder.

Conclusion: This study indicates that NaOH modified IC leaf powder has rapid adsorption rate and good adsorption capacity for lead. The Pb²⁺ adsorption was found to be dependent on initial lead concentration, contact time, pH, temperature and amount of adsorbent. The adsorption of lead was found to be fitted the Langmuir isotherm equation, which suggests monolayer coverage of adsorbent surface. Kinetic of lead adsorption obeyed the pseudo-second order model, which suggests chemisorption as the rate-determining step in adsorption process. Maximum adsorption of lead occurred at pH 5 and a higher adsorption rate occurred at lower temperature

(30 °C), indicating exothermic nature of adsorption. Since IC leaves are highly abundant and can be easily synthesized at relatively low cost, the adsorbent could be applied for the removal of lead from wastewaters.

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