Sorption Mechanism of Lead Ions From Aqueous Solution By Imperata Cylindrica Dried Leaf Particle: Effect of Temperatures

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Abstract

This study was conducted to investigate the sorption mechanism of Pb^{2+} *ions from aqueous solution onto Imperata cylindrica (IC) dried leaf particles. The effect of temperatures (30, 35 and 40*^{o}*C) was scrutinised from a batch adsorption system using a synthetic liquid waste containing* Pb^{2+} *ions. Adsorption of lead ions mechanism was investigated by intraparticle diffusion model. The results showed that higher adsorption rate occurred at higher temperature, and obeyed the pseudo second order adsorption model. The overall rate of lead uptake was found to be controlled by external mass transfer at the beginning of adsorption, then gradually changes to intraparticle diffusion controlled at a later stage. The intraparticle diffusion constant increased with increasing temperature. The values of effective diffusion coefficient (Di) increased at higher temperatures, which were 5.5466 ×* $^{10-9}$*, 6.8215 ×* 10^{-9}*, and 7.3726 ×* 10^{-9} m^2/s *at 30, 35, and 40 ◦C, respectively*

Keywords: *sorption, mechanism, Lead, Imperata cylindrica, diffusion*

Introduction

The presence of heavy metals in waters has been a major attention for researchers for years due to their toxicity towards aquatic life, human beings and the environment. Lead is one of the common toxic heavy metals widely discharged into the environment as liquid waste by metallurgical industry, electroplating and metal finishing industries, paint manufacture, storage battery manufacture, petroleum refining and drainage from ore mines in many developing countries. 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. Lead can also damage human nervous system and cause brain disorder. A long term exposure to lead may cause nephropathy, abdominal pains and particularly harmful to woman’s ability to reproduce (Bhatacharyya and Gupta, 2006). Excessive exposure of human body to lead may lead to anemia, mental retardation, coma, seizures and bizarre behaviour (Botkin and Keller, 2000). A number of investigations have been carried out to determine the best methods for the removal of metal ions from water such as chemical precipitation, ion-exchange, electrochemical deposition, solvent extraction and adsorption. Among these methods, adsorption has been proven as the most appealing in terms of economic and an environmental friendly procedure to remove heavy metals in wastewater with concentrations below 100mg.L^{-1} (Ahmad *et al*., 2009; Aksu, 2005). Adsorption of heavy metal using natural adsorbents or agricultural waste products 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. The use of agricultural wastes for the treatment of polluted water is also an attractive and promising option for the environment. A wide variety of agricultural waste materials such as Moringa oleifera bark (Reddy *et al*., 2010), sawdust (Rafatullah *et al*., 2009), Saraca indica leaf powder (Goyal *et al*., 2008), tree fern (Lalhruaitluanga *et a*l., 2010), Melocanna baccifera (bamboo) (Ho *et al*., 2004), and rice husk (Akhtar *et al*., 2010) are being used as low-cost alternatives to expensive adsorbents.

This paper reports the study on the effect of temperature on the sorption mechanism of lead onto Imperata cylindrica (IC) dried leaf particle based on intraparticle diffusion and pseudo second order equations. IC is a pernicious pest plant due its ability to easily colonize, spread and subsequently compete and displace desirable vegetation and disrupt ecosystems (Holm *et al*., 1977) wildly found in Africa, Asia, Australia and America. The potential of IC leaf as adsorbent is based on its hyperaccumulator structure in the mitochondria and

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plastids, which may adsorb and store metal ion under acidic condition (Amils *et al*., 2007).

Sorption Mechanism

Any adsorption process consists of different steps, the surface diffusion followed by intra-particle diffusion. In general, the adsorption was governed by the liquid phase mass transport or by intraparticle mass transport. The mass transfer rate can be expressed as a function of the square root of time (t). The intraparticle diffusion parameter, *k*i (mg/g min$^{0.5}$) is defined by the following expression (Werber Jr. and Morris, 1963):

$$q = k_i t^{0.5} + I \qquad (1)$$

Theoretically, the plot of *k*i versus $t^{0.5}$ should show at least four linear regions that represent boundary layer diffusion, followed by intraparticle diffusion in macro, meso, and micro pores (Ho and McKay, 1998). These four regions are followed by a horizontal line representing the system at equilibrium. For fully turbulent mixing, intra-particle diffusion is very high, and hence, it may be assumed that the transport of adsorbate molecules from the bulk solution to the adsorbent external surface through the boundary layer diffusion is rate determining. The change in concentration of lead with respect to time can be expressed by Mohan and Singh (2004):

$$-\frac{dC}{dt} = k_{sa}(C - Ce) \qquad (2)$$

At time t = 0, *Ce* = 0, thus equation (2) became:

$$\left[\frac{d\left(\frac{C}{Co}\right)}{dt} \right]_{t=0} = -k_{sa} \qquad (3)$$

The volumetric external mass transfer coefficient k_{sa} can be calculated from the slope of *C/Co* versus time *t* using the experimental kinetic data for the first initial rapid process of 5 min where the external mass transfer is dominant.

In order to determine the actual rate controlling steps in lead adsorption on IC leaf particles, the experimental data was further analysed using the following expression (Boyd *et al*., 1947):

$$Bt = -0.4977 - \ln[1 - (q/qe)] \qquad (4)$$

The transient behaviour of the system can be investigated by Ho's pseudo second order kinetic equation (Ho, 1995): $\frac{dq}{dt} = k_2 (q_e - q)^2$ (5)

Integrating equation (5) for boundary conditions *t* = 0 to *t* = *t* and *q* =0 to *q* = *q* gives:

$$q = \frac{{q_e}^2 k_2 t}{1 + q_e k_2 t} \qquad (6)$$

and the initial rate of adsorption $h_{o,2}$ is:

$$h_{o,2} = k_2 . q_e^2 \qquad (7)$$

Methodology

Adsorbent preparation

The IC leaves were collected from the surrounding area of Department of Chemical Engineering, Faculty of Engineering, Diponegoro University-Indonesia. The leaves were thoroughly washed with distilled water to remove dirt, dried in an oven at 105°C for a period of 24 hours, then ground and sieved to obtain the average particle size of 315 μm. The leaf particle was then stored in a desiccators prior for use as adsorbent.

Sorption Experiments

All chemicals used in the experiments were of analytical grade reagents. Lead nitrate (Sigma-Aldrich) was used as the source of Pb^{2+} and all of the solutions were prepared in distilled water. Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 100 mL capacity by agitating 0.1 g of the adsorbent with 25 mL of the 20 mg/L aqueous Pb^{2+} solution in a thermostatically controlled water bath shaker (Memmert GmbH + Co.KG, Model WB 10, Schwabach, Germany) at three different temperatures (30, 35 and 40°C), for a pre - determined time interval at a constant speed of 200 rpm. The initial pH of the solution was fixed at 4 by adding drops of 0.1 M HCl or NaOH solutions. After adsorption, the mixture was filtered through Whatman filter paper (No. 40). The concentrations of lead in the solutions before and after equilibrium were analysed by Atomic Absorption Spectrophotometer (Analyst 200 AA, Perkin Elmer, USA) using air-acetylene flame. All experiments were performed in triplicates and results were reported as average. The amount of Pb^{2+} adsorbed at time t, q (mg/g) was calculated by using the following expression:

$$q = \frac{[V(Co - C)]}{m} \qquad (8)$$

Results and Discussion

The adsorption kinetics of lead ion on the IC leaf particle was evaluated using pseudo second order model. The initial lead initial adsorption rate, $h_{o,2}$, adsorption rate constant, k_2, and equilibrium concentration of lead in the leaf particles, q_e are shown in Table 1.

Table 1. Pseudo Second Order Rate Constants at Initial Lead Concentration of 20 mg.L^{-1} and Different Temperatures

$T/^oC$	q_{exp}/ mg.g^{-1}	q_e/ mg.g^{-1}	k_2/ g.mg^{-1}.min^{-1}	$h_{o,2}$/ mg.g^{-1}.min^{-1}
30	3.6	3.69	0.0305	0.42
35	3.89	4.02	0.0337	0.55
40	4.1	4.28	0.0433	0.79

Figure 1 shows the intraparticle diffusion plots for the adsorption of lead onto leaf particle at different temperatures, *C*o 20 mg.L^{-1}, IC leaf particle dosage 4 mg.L^{-1}, and pH 4.

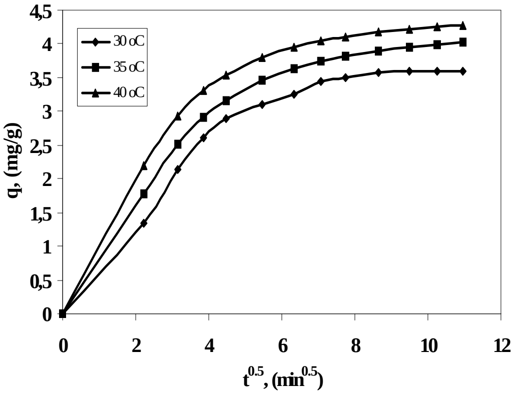

Figure 1. The intraparticle diffusion plot for lead adsorption on IC leaf particles at different temperatures with initial concentrations 20 mg.L^{-1}, pH 4 and leaf particle dose: 4 mg.L^{-1}.

It is observed from the figure that the start of the second linear region, where the rate is assumed to be controlled by intraparticle diffusion, is dependent on temperature. The intraparticle diffusion controlled region at 30 ◦C started after 15 min, while the time decreased with increasing temperature to be 10, and 6 min at 35 and 40 ◦C, respectively. This would be expected due to the decreased viscosity of aqueous lead solution, and also the effect of heating on increasing the diffusion of molecules in solution. Both factors enhance the diffusion of lead through the boundary layer, therefore, the initial film-diffusion controlled time period becomes shorter at higher temperatures. It can also be seen from Table 2 that the values of the intraparticle diffusion constant increase with increasing temperature. The values of *k*i are 0.2936, 0.3060, and 0.3114 mg.g^{-1}.min$^{0.5}$ at temperatures 30, 35, and 40◦C, respectively. This is probably due to the swelling of fibers at higher temperatures, which facilitates lead ions diffusion inside the adsorbent particle.

Table 2. Diffusion Coefficient for Adsorption of Lead Onto IC Leaf Particle at Different Temperatures, pH 4 and Initial Lead Concentration 20 mg.L^{-1}

$T/^oC$	*I*	*k*i/mg.g^{-1}. min$^{-0.5}$	k_{sa}/ min^{-1}	*D*i× 10^9/ m^2.s^{-1}
30	1.0190	0.2936	0.2188	5.5466
35	1.2579	0.3060	0.2192	6.8215
40	1.5357	0.3114	0.2220	7.3726

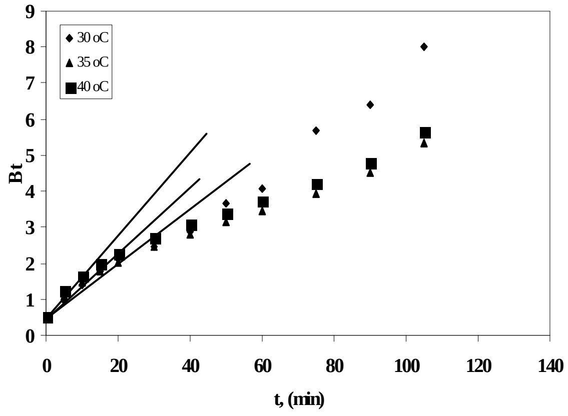

Figure 2. Boyd plots for lead adsorption at 30, 35 and 40^{o}C with initial lead concentration 20 mg.L^{-1}; pH 4 and IC leaf particle dose: 4 mg.L^{-1}.

The volumetric external mass transfer coefficient k_{sa} was calculated from the slope of *C/Co* versus time t using the experimental kinetic data for the first initial rapid process of 5 min where the external mass transfer was dominant. The values of initial adsorption rates, k_{sa} (min^{-1}), are shown in Table 2. It is observed that the adsorption rate in the initial period, where external mass transfer is assumed to predominate, increases with increasing temperature. The relationship between k_{sa} and *T* (◦C) fits the equation:

$$k_{sa} = 0.2668 - 0.0030T + 5.003 \times 10^{-5}T^2 \qquad (9)$$

The plots of *Bt* against time at different temperatures are shown in Figure 2 and the values of *D*i are presented in Table 2. It is observed from the figure that the plots are linear in the initial period of adsorption, with the time duration of the linear period decreasing with increase of temperature. The initial adsorption period, assumed to be controlled by external mass transfer lasted for 15, 10, and 6 min at temperatures 30, 35, and 40 ◦C, respectively. It is also observed in Table 6 that the values of *D*i increase at higher temperatures, so that *D*i values are 5.5466 × 10^{-9}, 6.8215 × 10^{-9}, and 7.3726 × 10^{-9} m^2/s at 30, 35, and 40 ◦C, respectively

Conclusions

The adsorption rate of lead ion onto IC leaf particles occurred faster and more at higher temperature, and obeyed the pseudo second order adsorption model. The overall rate of lead uptake was found to be controlled by external mass transfer at the beginning of adsorption, then gradually changes to intraparticle diffusion controlled at a later stage. The intraparticle diffusion constant increased with increasing temperature.

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Nomenclatures

Bt = adsorption controlling rate indicator (eq.4)
Co = initial Pb^{2+} concentrations, mg. L^{-1}
C = Pb^{2+} concentrations at time t, mg. L^{-1}
Ce =Pb^{2+} concentrations at equilibrium, mg. L^{-1}
Di =effective diffusion coefficients,$cm^2.s^{-1}$
$h_{o,2}$ = initial adsorption rate,mg. min^{-1}
I = intercept eq. (1)
k_i = the intraparticle diffusion constant, mg. g^{-1} $min^{-0.5}$
k_2 = adsorption rate constant,g.(mg $min)^{-1}$
k_{sa} =volumetric external mass transfer coefficient, min^{-1}
m = mass of the adsorbent, g.
q = Pb^{2+} adsorbed at time t, $mg.g^{-1}$
q_e = Pb^{2+} adsorbed at equilibrium, $mg.g^{-1}$
t = time, min.
V = volume of the aqueous phase, L

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