Intraparticle Diffusion in Lead Adsorption Onto Paper and Pineapple Wastes as Adsorbents

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ABSTRACT

The paper wastes from paper processing and pineapple wastes from pineapple juice processing were used as adsorbents for removal of lead by adsorption. The adsorption rates for the two systems were determined, and the adsorption mechanism was shown to be predominantly intraparticle diffusion. For a given adsorbent, an increase in the initial feed lead concentration resulted in an increase in the adsorption rate. The results showed that increasing the lead ion concentration in aqueous solution would increase the diffusion of metal ions in the boundary layer and to enhance the diffusion in the solid. The potential use of paper and pineapple wastes as a cost-effective adsorbent for lead removal in wastewater treatment was demonstrated.

Keywords: *Lead adsorption, Paper waste, Pineapple waste, Intraparticle diffusion*

1. INTRODUCTION

Industrial wastewater effluent containing heavy metals causes serious environmental problems because of the toxicity and assimilation of heavy metals in organisms. Thus safe and effective treatment of wastewater containing heavy metals becomes a challenging task for us and in the industry as a whole due in part to the fact that cost-effective treatment alternatives are not available [1]. Lead is one of the most toxic heavy metals and its distribution in the environment, either aquatic or atmospheric, imposes a health hazard [2]. At present, lead is still used as industrial raw materials for batteries, printing, pigments, fuels, photographic materials, and explosive manufacturing [3] – [4]. A number of methods have been proposed to remove toxic heavy metals from aqueous solutions. Chemical precipitation has traditionally been employed to remove heavy metals from wastewater. However, this process has several disadvantages: The presence of complex ligands in wastewater may hinder metal hydroxide precipitation and result in residual metal concentrations, making it difficult to meet the increasingly stringent standards for effluent discharge [5]. Adsorption has been shown as a feasible alternative method for removing heavy metals from wastewater, and several natural and synthetic hydrous solids have been investigated for use as potential adsorbents for heavy metals. Among these, metal oxides [6] – [8] and activated carbon [9-10] are the most commonly employed, but the high costs of these materials limit their large-scale use for removal of metals [11]. Therefore, there has been a great deal of effort in developing low cost adsorbents, including fly ash [12] – [13], peats [14], activated sludge [15], waste slurries, and biosorbents [16].

In this work, the utilization of paper waste sludge from paper processing as an adsorbent to remove lead from wastewater was proposed. Pulp and paper industry generates a large quantity of waste sludge from the paper recycling process, which causes a significant disposal problem. Such waste sludge has properties similar to those of other sludge such as municipal waste sludge [17] or wine processing waste sludge [18], and it is thus expected to be capable of adsorbing heavy metals. Efforts had been made in this study to adsorb lead ions from aqueous solutions, and the adsorption characteristic was investigated. In addition, pineapple waste from pineapple juice processing was also studied as an adsorbent for lead removal from aqueous solutions.

2. RESEARCH METHODOLOGY

Paper waste sludge was obtained from the final recycle paper processing plant located in Samutpragran (Thailand). The sludge was washed with distilled water to remove easily suspended materials and dried in an oven at 105 °C for 48 h. The prepared sludge was kept in desiccators. All chemicals used in the experiments were analytical grade and distilled water was used to prepare all solutions. Pineapple-waste was obtained from the solid waste of filtration process in a pineapple juice plant located in Prajuabkirikhun (Southern of Thailand). The pineapple-waste was washed with distilled water to remove suspended materials many times and finally dried in oven at 105 °C for 48 h.

The adsorption experiments were carried out at lead nitrate concentrations of 100, 150, 200 and 250 ppm (equivalent to lead ion concentrations of 62.5, 93.8, 125.1 and 156.4 ppm, respectively), pH 6, waste sludge 5 g L^{-1} and adsorbent particle size of 50-100 μm, and temperatures of 30, 40 and 50 °C. In the batch adsorption experiments, the time required to reach adsorption equilibrium was about 2 h, and the samples were withdrawn periodically for analysis with an atomic adsorption spectrophotometer (Varian model SpectrAA-300) after Filtration through a 0.45 μm membrane filter.

3. RESULTS AND DISCUSSION

3.1 Characterization of paper waste sludge

The specific surface area (BET) of paper and pineapple wastes measured by the Micromeritic Chemisorb 2750 automated system were 205 and 45 m^2/g, respectively. A major element in the paper and pineapple is cellulose, which contains hydroxyl (R-OH) groups that can serve as coordination and/or electrostatic interaction sites for sorption of heavy metals, as illustrated below

$$\text{R-OH} + \text{Pb}^{2+} \rightleftharpoons \text{R-O-Pb}^{+} + \text{H}^{+} \quad (1)$$

3.2 Adsorption efficiency and adsorption capacity

The adsorption efficiency of lead ion was calculated from

$$\%\,\text{adsorption efficiency} = \left(\frac{C_0 - C_e}{C_0}\right) \text{x}\, 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium (final) concentrations (ppm) of lead in the solution.

The adsorption capacity of lead ion can be analyzed based on the mass balance according to

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

where q_e represents the amount of lead ion adsorbed per unit mass of adsorbent (mg metal/g of dry adsorbent), V is the volume of solution (L), and m is the mass of the dry adsorbent (g).

The experimental data showed that the adsorption capacities to lead ions increased with an increase in the initial lead concentration in the range of 100-250 ppm when the paper waste was used as adsorbent. However, there was a decrease in the adsorption efficiency. A maximum adsorption efficiency of around 90 % was achieved at a lead concentration of 100 ppm, as shown in Fig. 1. The adsorption capacities and adsorption efficiencies for lead ion onto pineapple waste were shown in Fig. 2, and a similar trend was observed with respect to sorption capacity and efficiency. The maximum lead adsorption efficiency onto pineapple waste was about 80 % at a lead concentration of 150 ppm. For both adsorbents, the temperature did not exhibit a significant effect on the sorption characteristics.

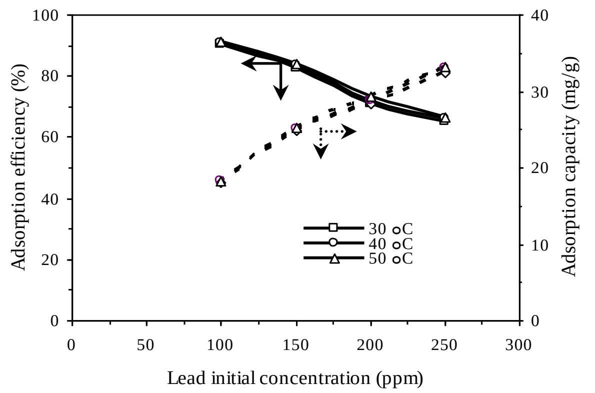

Fig.1 *Adsorption efficiency and adsorption capacity onto paper waste with different lead concentrations and temperatures at pH = 6.*

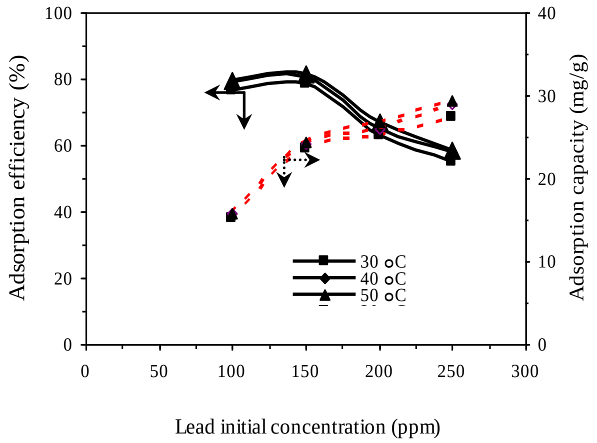

Fig.2 *Adsorption efficiency onto pineapple waste with different lead concentrations and temperatures at pH= 6*

3.3 Intraparticle diffusion

The mechanism of adsorption is generally considered to involve three steps: (i) mass transfer across the external boundary film of liquid surrounding the outside of the particle; (ii) adsorption at active sorption sites on the surface (internal or external) and the binding process may be physical or chemical; this step is often assumed to be extremely rapid; (iii) diffusion of the adsorbate molecules from one adsorption site to another either by diffusion through the liquid-filled pores or by surface diffusion mechanism. One or more of the steps can be rate-controlling that determine the overall adsorption mechanism.

The intraparticle diffusion model of Webi and Chakravort [19] was used in this work. The fractional approach to equilibrium varies according to a function of $(D_t/r^2)^{1/2}$, where D_t is the diffusion coefficient in the solid and r is the particle radius [20]. The initial rate of intraparticle diffusion of lead in the waste sludge can be expressed as

$$q_t = k_{id} t^{1/2} \quad (4)$$

where q_t is the amount of lead ion adsorbed (mg/g) at time t (min). Plotting q_t versus $t^{1/2}$ will give a straight line with a slope that is related to the intraparticle diffusion coefficients (k_{id}). Figs. 3-6 show the experimental data of q_t as a function of $t^{1/2}$ at different initial lead concentrations and temperatures for both adsorbents. These plots have the same general trends: an initial curved portion followed by a linear portion and a plateau. The shape of the plots is similar to those reported by Li et al. [18]. The initial curved portion is attributed to bulk diffusion, a linear portion to the intraparticle diffusion and the plateau to the sorption equilibrium.

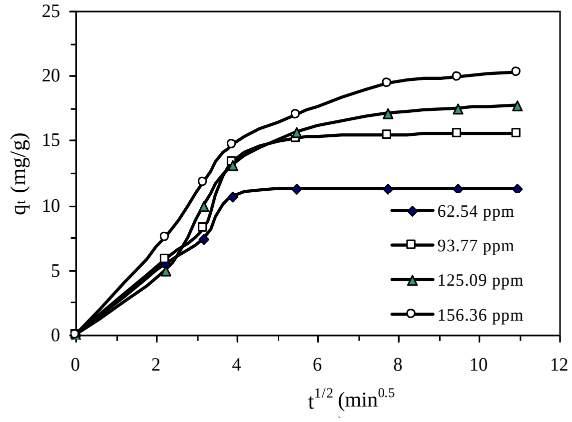

Fig.3 *Intraparticle diffusion plot for lead adsorption at different initial concentrations. pH 6, paper waste 5 g/L and temperature 30 ℃.*

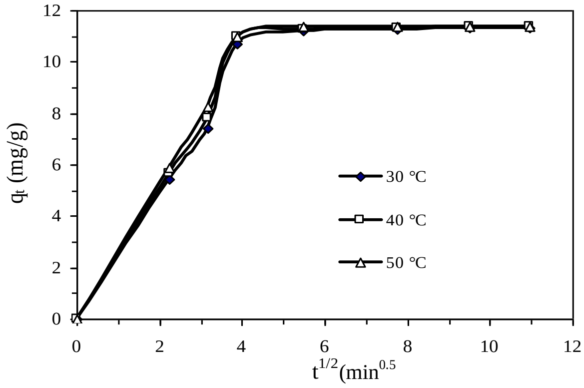

Fig.4 *Intraparticle diffusion plot for lead adsorption at different temperatures. $PbNO_3$ concentration 100 ppm, pH 6, and paper waste 5 g/L*

As shown in Figs. 3-6, the q_t versus $t^{1/2}$ plots were not linear during the entire course of adsorption, implying that the adsorption is affected by more than one process steps. It may be postulated that two steps took place during lead sorption: First, a sharper portion that was attributed to the diffusion of lead ions through the solution to the external surface of adsorbent (i.e., diffusion of solute molecules in the boundary layer), and then a second portion that was related to the gradual adsorption stage, where intraparticle diffusion was the rate limiting step until an adsorption equilibrium was eventually reached. This is illustrated in Figs 7-10, which also show similar pattern on the effects of initial lead concentration and temperature on the adsorption characteristics with paper and pineapple wastes as adsorbents.

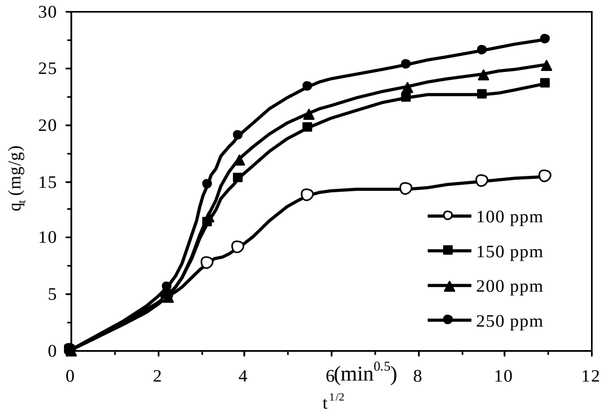

Fig.5 *Intraparticle diffusion plot for lead adsorption at different initial concentrations. pH 6, pineapple waste 5 g/L and temperature 30 ℃*

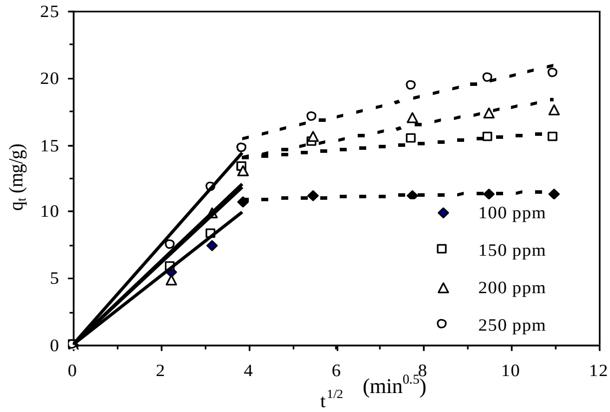

Fig.7 *Data fitting for intraparticle diffusion of lead ion onto paper waste at different initial lead concentrations and at pH 6 and 30 ℃*

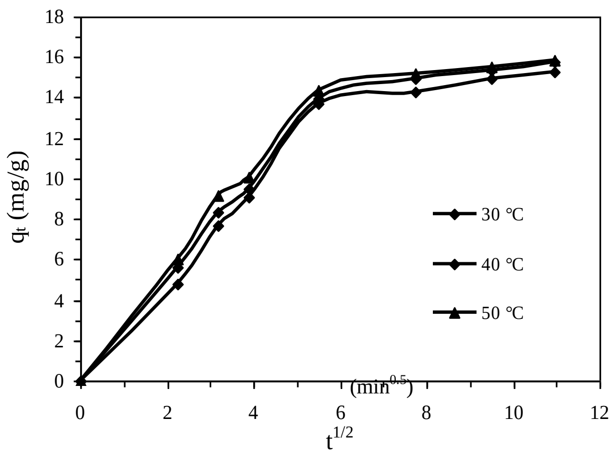

Fig.6 *Intraparticle diffusion plot for lead adsorption at different temperatures. $PbNO_3$ concentration 100 ppm, pH 6, and pineapple waste 5 g/L*

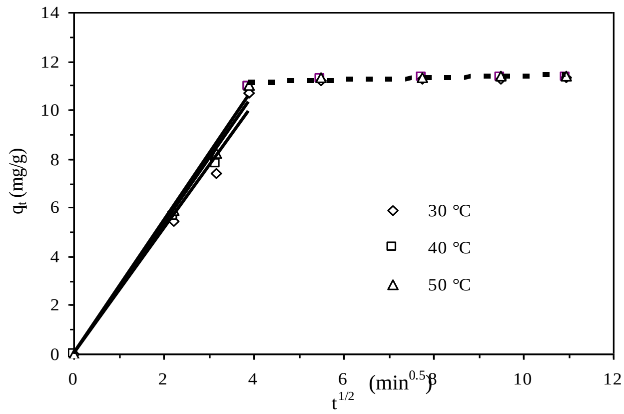

Fig.8 *Data fitting for intraparticle diffusion of lead ion onto paper waste at different temperatures and at pH 6 and 100 ppm*

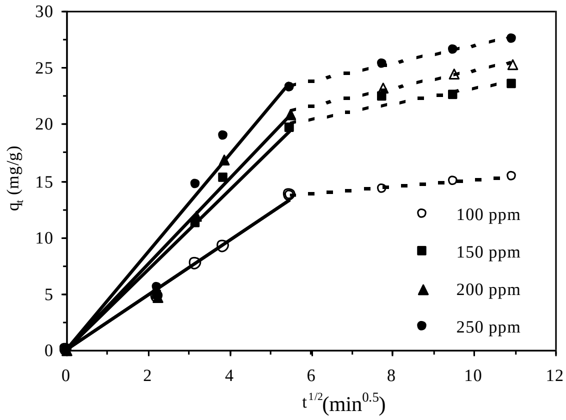

Fig.9 *Data fitting for intraparticle diffusion of lead ion onto pineapple waste at different initial concentrations and at pH 6 and 30 ℃*

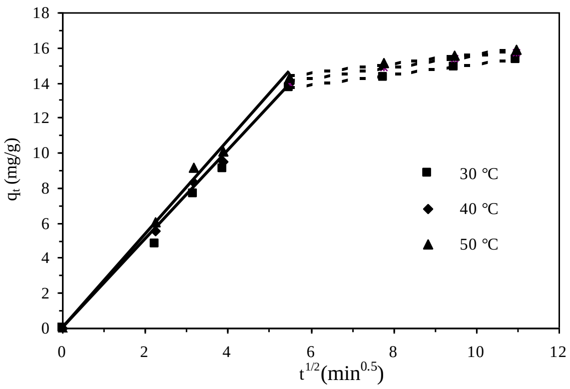

Fig.10 *Data fitting for intraparticle diffusion of lead ion onto pineapple waste at different temperatures and at pH 6 and 100 ppm*

The k_{id} values under these different conditions were calculated from the slopes of the linear portion of the curves. Table 1 to Table 4 list the k_{id} values at different initial concentrations of lead and temperatures with pH 6 and waste sludge of 5 g/L for paper and pineapple adsorbent, respectively. An increase in the initial lead ion concentration results in an increase in the intraparticle diffusion rate, and a higher operating temperature also enhances the diffusion coefficient.. The increased k_{id} values with increasing initial lead concentration can be explained by the growing effect of the driving force for lead sorption, which is the concentration gradient. At a higher temperature, the lead ions are more energetic for adsorption, and in the meantime the chain movement of cellulose in the adsorbent is also enhanced, both contributing to facilitated diffusion.

Table 1 *Intraparticle diffusion rate constants at temperature 30℃ and different initial $PbNO_3$ concentrations and with paper waste as adsorbent*

Conc. (ppm)	Paper Waste			
	$k_{id,1}$ $(1/min^{0.5})$	$k_{id,2}$ $(1/min^{0.5})$	R_1^2	R_2^2
100	2.571	0.071	0.981	0.625
150	3.034	0.257	0.946	0.617
200	3.111	0.609	0.948	0.851
250	3.700	0.782	0.994	0.913

Table 2 *Intraparticle diffusion rate constants at temperature 30℃ and different initial $PbNO_3$ concentrations and with pineapple waste as adsorbent*

Conc. (ppm)	Pineapple Waste			
	$k_{id,1}$ $(1/min^{0.5})$	$k_{id,2}$ $(1/min^{0.5})$	R_1^2	R_2^2
100	2.417	0.297	0.993	0.996
150	3.540	0.679	0.953	0.896
200	3.797	0.794	0.935	0.981
250	4.327	0.764	0.938	0.993

Table 3 *Intraparticle diffusion rate constants at $PbNO_3$ concentration 100 ppm and different temperatures with paper wastes as adsorbent*

Temp. (°C)	Paper Waste			
	$k_{id,1}$ $(1/min^{0.5})$	$k_{id,2}$ $(1/min^{0.5})$	R_1^2	R_2^2
30	2.571	0.071	0.981	0.625
40	2.662	0.046	0.986	0.670
50	2.729	0.045	0.994	602

Table 4 *Intraparticle diffusion rate constants at $PbNO_3$ concentration 100 ppm and different temperatures with pineapple wastes as adsorbent*

Temp. (°C)	Pineapple Waste			
	$k_{id,1}$ $(1/min^{0.5})$	$k_{id,2}$ $(1/min^{0.5})$	R_1^2	R_2^2
30	2.417	0.298	0.993	0.996
40	2.537	0.323	0.998	0.984
50	2.671	0.275	0.994	0.977

As mentioned earlier, the whole adsorption process could be explained by boundary layer diffusion, which determined the initial portion of the process, and intraparticle diffusion that determined the subsequent portions. If the intraparticle diffusion was the only rate-controlling step, the plot would pass through the origin; otherwise the boundary diffusion would also play a role on the adsorption to some degree. It could be deduced that there were three steps that controlled the rate of lead adsorption but only one was dominating in a particular time frame. The slope of the linear portion indicated the rate of the adsorption, and a smaller slope corresponded to a slower adsorption process. One could observe that the diffusion from the bulk phase to the exterior surface of adsorbent, which started at onset of the process, was the fastest. The adsorption at the active sorption sites on the adsorbent surface is generally considered to be extremely rapid, and then the diffusion of lead ions to an adsorption site either by diffusion through liquid-filled pores or by surface diffusion was shown to be slower as suggected by the smaller slope for the second portion of plots. This implied that the intraparticle diffusion of lead ions into micropores was the rate-limiting step in the adsorption process on paper and pineapple wastes, particularly over a long period of time. Moreover, the data shown in Figs. 7-10 also suggest that the rate of adsorption in micropores was comparable for both adsorbents. As seen in Table 1 to Table 4, there were differences in the slope of the first and second portions of the plots for both adsorbents. Comparing the plots of different initial concentrations and temperatures, the slopes of first portions of the plots were higher, which corresponded to an enhanced diffusion of lead ions from the exterior surface of adsorbent to the macropores and micrpores of the adsorbent, respectively.

4. CONCLUSION

This study showed that the paper and pineapple wastes could be used as the effective adsorbents for lead ions in wastewater treatment. The adsorption capacity and efficiency of the adsorbents were determined experimentally. The intraparticle diffusion model of Webi and Chakravort gave a good fit to the experimental results. The paper and pineapple wastes were shown to be promising cost-effective adsorbent to remove heavy metals from wastewater.

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