Adsorption of Cadmium and Lead Heavy metals by Chitosan Biopolymer: A Study on Equilibrium Isotherms and Kinetics

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Abstract— **Since heavy metal pollution is a significant aspect to aquatic ecosystems, the objective of this research work was to investigate adsorption characteristics of chitosan as an alternative adsorbent material. In this study, chitosan, synthesized from locally available shrimp type "penaeus monodon" was used to observe adsorption characteristics of cadmium (Cd) and lead (Pb) heavy metals from aqueous solution. Batch kinetic experiment studies were conducted for changing initial pH, initial concentration of metal ions, particle size and degree of deacetylation (DD) of chitosan. Simplified models such as, pseudo first order, pseudo second order and intra-particle diffusion models were used to analyze the experimental data. The result showed that the adsorption capacity strongly depends on pH and DD. It was clearly seen that higher adsorption of heavy metals occur at comparatively high pH and high DD. Equilibrium experimental data were analyzed by using two different isotherm models namely, Langmuir and Freundlich. The characteristic parameters for each isotherm and related correlation coefficients were determined by using mathematical modeling software. Isotherms show that adsorption process of Cd and Pb is a heterogeneous process.**

Keywords— Adsorption; chitosan; degree of deacetylation; isotherm

I. INTRODUCTION

The waste water from the industry is a significant danger to the aquatic ecosystems in all over the world. In Sri Lanka many rivers, water streams, wet lands and inland reservoirs have already been polluted with organic and inorganic substances like heavy metals, pesticides, colored substances, nutrients from fertilizers and solid particles [1]. Heavy metal pollution is momentous aspect to aquatic ecosystems due to these heavy metals are potentially toxic even at very trace amounts and they tend to bio accumulate [1, 2]. Due to these reasons, there is a great interest in removal of heavy metals from wastewater effluents. There are number of conventional methods available to remove heavy metals from wastewater including ion exchange, precipitation, filtration, membrane technology, reduction, etc., [3]. But, some of those methods are not efficient and some of those are very expensive. To overcome from those problems most researchers are focus in to the synthesis of low cost adsorbent from agricultural residues or industrial by products like palm kernel husk, corn cobs, wool, apple residue, olive mill products, banana husks, pine bark, sawdust, algae, etc. [4]. In this study, chitosan was synthesized by using shrimp waste from local shrimp processing factories.

Chitosan is a linear polysaccharide, composed of *glucosamine* and *N-acetyl glucosamine* units linked by *β (1-4) glycosidic* bonds. Chitosan shows good chelating ability with metals [5]. Degree of deacetylation (DD) is an important parameter in chitosan because of it directly measures the number of available amine groups in chitosan structure. The adsorption metals by micro porous solids such as chitosan can be analyzed using the results of kinetics and equilibrium experiments. Initial pH of the solution, physiochemical conditions, particle size, degree of deacetylation (DD) and agitation rate are profoundly affect to the adsorption process.

The objective of the present study was to investigate the possible use of chitosan as an alternative adsorption material for removal of cadmium and lead from waste water. Batch experiments were carried out for kinetic and equilibrium studies on removal of cadmium and lead ions from aqueous solution. The influence of DD of the chitosan, initial pH of the metal ion solution, particle size and initial metal ion concentration of the solution were studied. Pseudo first order model, pseudo second order model and intra-particle model were used to evaluate the mechanism of adsorption process. Adsorption equilibrium data were analyzed by using three different isotherm models; Langmuir, Freundlich and Dublin-Radushkevich model.

II. MATERIALS AND METHODS

A. Adsorbent

Shrimp shells were collected from local shrimp processing factory in Western province, Sri Lanka and chitosan was synthesized in laboratory scale from that shrimp waste. 250-75

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mesh size particles of chitosan were taken for the adsorption studies. Two DD values of the chitosan were obtained by changing process parameters.

B. Adsorbate

Stock solutions (1000mg/L) of Cd^{2+} and Pb^{2+} ions were prepared by dissolving required amount of analytical grade $CdSO_4$ and $Pb(NO_3)_2$ in deionized water. Stock solutions were diluted with deionized water to obtain desired concentration ranging from 5 to 1000 mg/L.

C. Characteriation of Chitosan

DD of the chitosan samples were calculated by using Fourier transform infrared spectroscopy (FTIR) KBr pellet method.

D. Analysis

The concentrations of remaining heavy metal in experimental solutions were measured by using GBC 932 PLUS atomic adsorption spectrophotometer (AAS).

E. Adsorption Experiment

Adsorption experiments were conducted by varying contact time, initial pH, chitosan dose, initial heavy metal concentration under the aspect of adsorption kinetics. Adsorption experimets were carried out in 100ml conical flasks and the total volume of the solution was kept at 50ml. The initial pH of the solution was controlled by adding 0.1 M NaOH and HCl solutions. For the kinetic studies, the mixture was agitated at 300rpm at room temperature for time interval ranging from 5minutes to 300 minutes. At predetermined time, the flasks were removed from the shaker and filtered the chitosan powder. The remaining metal ion concentration was measured by using AAS technique. For equilibrium isotherm studies, 50ml heavy metal solutions were shaken at 300 rpm for 180 minutes at room temperature and the concentration of heavy metal was 5 to 1000 mg/L.

The amount of metal adsorbed at equilibrium was calculated by the equation (1):

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

Where m is the mass of the chitosan (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mg/L), C_e is the equilibrium metal concentration (mg/L) and q_e is the metal quantity adsorbed at equilibrium (mg/g) [4,6,7].

F. Adsorption Isotherms

1) Langmuir isotherm : This model has been widely used for the adsorption of heavy metals, oraganic pollutants, dyes, etc. This isotherm assumes homogeneous monolayer adsorption and also assumes all the adsorption sites have same affinity and the adsorption of one site does not affect to the adsorption at adjacent site. The linear form of Langmuir equation is given in equation (2);

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right) C_e \tag{2}$$

Where, b is adsorption equilibrium constant (L/mg) and q_e is the amount adsorbed on unit mass of the adsorbent (mg/g) and C_e is the equilibrium concentration and Q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mg/g) [8,9].

Linear relationship of C_e/q_e versus C_e plot indicates the Langmuir equation is obeyed by adsorption equilibrium. Further, a dimensionless equilibrium parameter, R_L, also known as the separation factor can be defined as equation (3);

$$R_L = \frac{1}{1 + bC_o} \tag{3}$$

For favorable adsorption, the value of R_L lies between 0 and 1 and $R_L > 1$ represents an unfavorable adsorption. If R_L = 1, it represent linear adsorption and if R_L = 0, it gives irreversible adsorption [4].

2) Freundlich isotherm : This isotherm applies to adsorption on heterogeneous surface and it consider the intercation between adsorbed molecules. The linear form of Freundlich isotherm is given in equation (4);

$$\log q_e = \log K_f + (1/n) \log C_e \tag{4}$$

Where, K_f is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n is a measurement of deviation from linearity. If the value of n is equal to unity, the adsorption is liner; if the value is below unity, implies that adsorption process is chemical; if value is above unity adsorption is a favorable physical process [9,10].

G. Adsorption Kinetics

The kinetic parameters are important in predicting the adsorption rate which can be used as important information for designing and simulating real adsorption operation. To identify the rate controlling mechanism during the adsorption of heavy metals, three steps were considered;

- Mass transfer of the metallic ion from the bulk solution to the chitosan surface
- Adsorption of the metallic ions into sites
- Internal diffusion of the metallic ions into chitosan

Simplified models like pseudo first order model, pseudo second order model and intra-particle model were used evaluate the experimental data.

1) Pseudo first order kinetics: The non-linear form of pseudo first order equation is given by equation (5);

$$\frac{dq}{dt} = K_1 (q_e - q) \tag{5}$$

Where q_e and q are the amounts of heavy metals adsorbed at equilibrium time and at any instant time respectively, and K_1 is the rate constant for the pseudo first order adsorption. By

integrating the equation (5) with boundary conditions of q=0 and q=q_e, equation (6) can be obtained.

$$q=q_e(1-e^{K_1 t}) \quad (6)$$

Adsorption capacity, q versus time, t graph was plotted according to the above equation and pseudo first order rate constant and linear regression (R^2) were calculated.

2) Pseudo second order kinetics: The non-linear form of pseudo second order equation is given by equation (7);

$$\frac{dq}{dt}=K_2(q_e-q)^2 \quad (7)$$

Where K_2 is the rate constant for the pseudo second order adsorption and other variables are same as in equation 8. By integrating the equation (7) with boundary conditions of q=0 and q=q_e, equation (8) can be obtained;

$$q=\frac{K_2 q_e^{\,2} t}{(1+K_2 q_e)} \quad (8)$$

Adsorption capacity, q versus time, t graph was plotted according to the above equation and pseudo second order rate constant and linear regression (R^2) were calculated.

3) Intra particle diffusion model: According to the Fickian diffusion law, the amount of adsorption by diffusion controlled dynamics as a function of time can be given by equation (9);

$$q=2C_0 S\sqrt{Dt/\pi} \quad (9)$$

For analytical convenience equation (9) can be rewritten as following equation (10);

$$q = K_i t^{0.5} \quad (10)$$

Where K_i is the intra-particle diffusion rate constant and q is the amount of metal adsorbed at any given time [11].

III. RESULTS AND DISCUSSIONS

A. Characterization of Chitosan

The adsorption capacity of chitosan depends upon the amine group percentage of the chitosan, directly measures by the degree of deacetylation (DD). DD was depend on the processing parameters of the chitosan extraction process, such as concentration of NaOH, temperature, number of times of deacetylation etc,. Since DD is a structural variation in the chitosan molecule, it can be clearly observed through the FTIR spectroscopy.

The main characteristic peak in chitosan FTIR is C=O stretching of acetyl amide group which is around 1655 cm^{-1}. During the deacetylation process these acetyl amide (-NHCO) groups were converted in to the amine ($-NH_2$) groups. According to the Figure 1, the characteristic peak for the C=O stretching, find in 1650 cm-1, shows significant reduction in high DD sample implying more C=O bonds converted in to NH2 and resulted in low intensity peak.

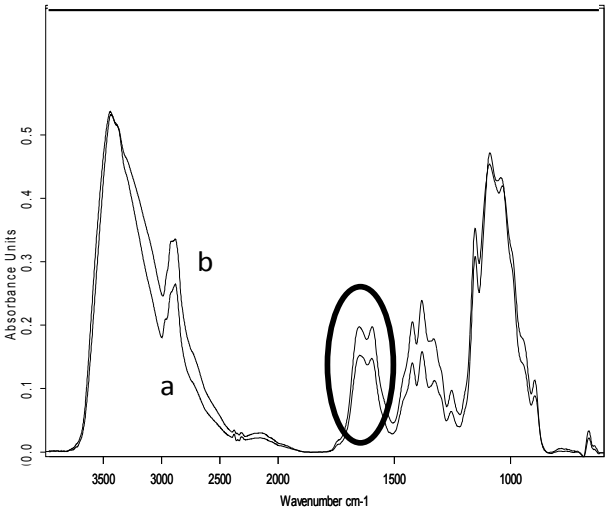

Fig 1. FTIR spectrum of chitosan (a) High DD sample (b) Low DD sample

B. Effect of contact time

The effect of contact time on Cd(II) and Pb(II) adsorption on chitosan was studied to investigate the rate of metal removal. Figure (3) shows the percentage removal of Cd and Pb heavy metals at two different metal ion concentrations. The rate of removal of metal ion is increased rapidly upto 120 minutes and the further increase in the contact time has a little impact on the rate of adsorption.Contact time is an important parameter because this factor determines the adsorption kinetics of an adsorbate at a given initial concentration of the adsorbate.

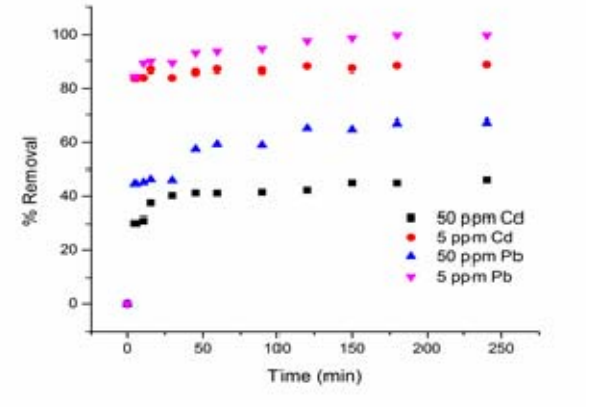

Fig. 2 Effect of contact time initial metal ion concentration on adsorption process

C. Effect of initial metal ion concentration

Cd and Pb adsorption is significantly influenced by the initial concentration of the metal ion solutions. In this study two different concentrations (5 ppm and 50 ppm) of Cd and Pb solutions were used at a room temperature. The results show that with an increase in the heavy metal concentration from 5 mg/L to 50 mg/L, the percentage of removal of Cd decreases from 88.48% to 46.25% and the percentage of removal of Pb decreases from 99.84% to 67.36%. This reduction is due to the limited number of active sites available in chitosan, which would become saturated after some particular concentration. Figure 2 shows this behaviour.

D. Effect of Degree of Deacetylation (DD)

According to the Figure 3, DD was significantly affected to the adsorption capacity of chitosan. At high DD, nearly 46% of Cd and 67% Pb was adsorbed in to chitosan while in low DD 35% of Cd and 56% Pb was adsorbed. The reason for this is number of amino groups in chitosan sample and that amino groups are facilitated to adsorb more heavy metal ions from the solution.

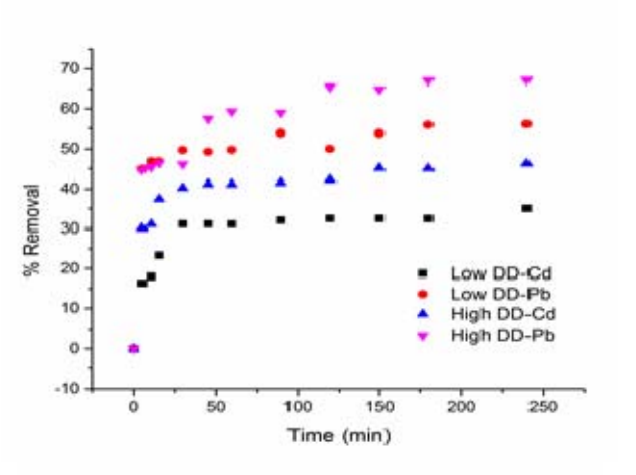

Fig. 3 Effect of DD on the adsorption of Cd and Pb

E. Effect of pH

Initial pH of the solution is an important parameter in the adsorption of heavy metals. In the present work, increase in the pH was restricted by the formation of $Cd(OH)_2$ and $Pb(OH)_2$ precipitates. Due to that reason for Cd, pH range 3 to 6.5 was used as low and high values and for Pb, pH range 2 to 4.5 was used as low and high pH values. According to the Figure 4, at 50mg/L concentration, nearly 50% of Cd and 67% of Pb were absorbed in to chitosan at high pH and nearly 19% of Cd and 48% of Pb were absorbed in to chitosan at low pH. It can be clearly observed that the adsorption capacity was increased with the increasing pH values.

The low adsorption capacity in acidic solution can be explained by the competition between protons and metallic ions for available amino adsorption sites, and by electrostatic repulsion. The following reaction shows the influence of pH on the uptake of metallic ions;

$$Chito - NH_3^+ + M^{2+} \leftrightarrow Chito - NH_2 - M^{2+} + H^+$$

The equilibrium of this reaction is shifted to the left at higher H^+ ion concentrations (lower pH), reducing the number of binding sites for metallic ions. In addition, the protonation of electrostatic repulsion of metal cations that reduces number of binding sites available for metallic ions [6].

On the other hand, at higher pH, there is a decreased in H^+ ions and that shifted to the reaction right and both competition for binding sites and electrostatic repulsion are reduced. Therefore adsorption performance is improved.

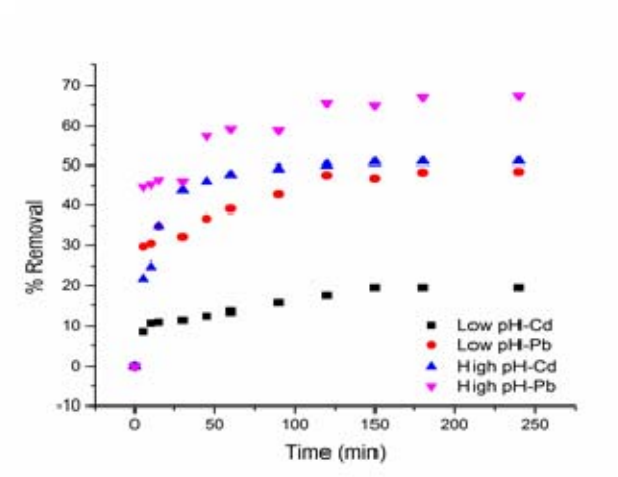

Fig. 4 Effect of pH on the adsorption of Cd and Pb

F. Effect of Particle size

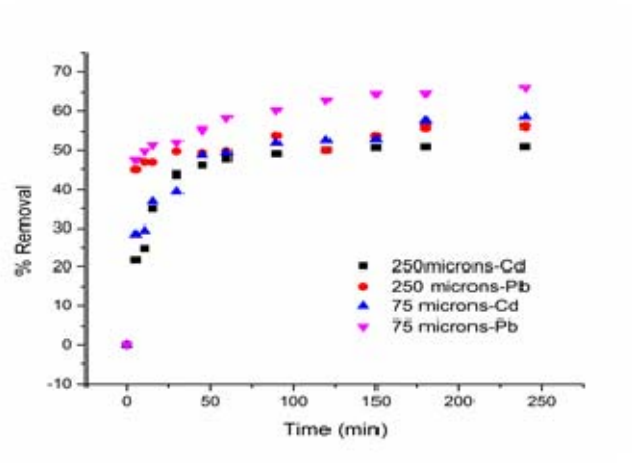

Fig. 5 Effect of particle sizes on the adsorption process

According to the Figure 5, it can be clearly observed that the adsorption capacity increased with the reducing particle size. But, the increment is not very significant like in pH variation. Therefore it can be concluded that the particle size affect to the adsorption process but, it is not a significant factor for adsorption of heavy metal ions.

G. Adsorption isotherm study

1) Langmuir isotherm:

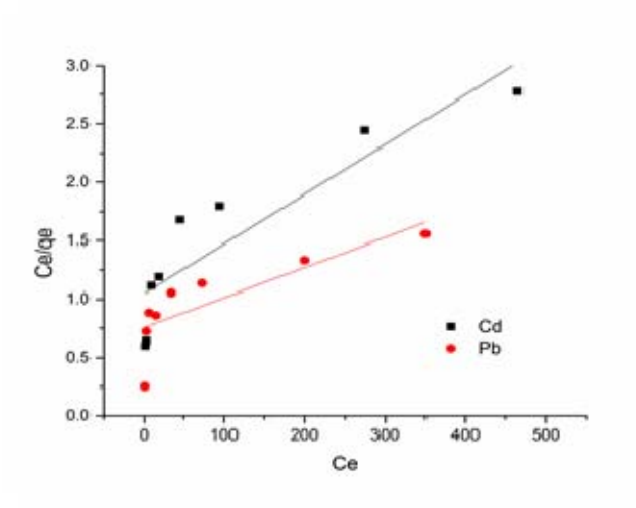

Fig. 6 Langmuir isotherm model for adsorption

According to the Figure 6, coefficients of determination obtained from the results were low. (for Cd; R^2=0.787 and for Pb; R^2=0.6122). Therefore this adsorption is not completely governed by the Langmuir isotherm and adsorbent surface is not completely homogeneous and adsorption affinity is different for different active sites. However, the dimensionless parameter, R_L, which is a measure of adsorption favourability, is found in the range of 0.98 to 0.2 ($0<R_L<1$) for both Cd and Pb which confirms the favourable adsorption process. Since $R_L>0$, it also confirms reversible adsorption process.

2) Freundlich Isotherm:

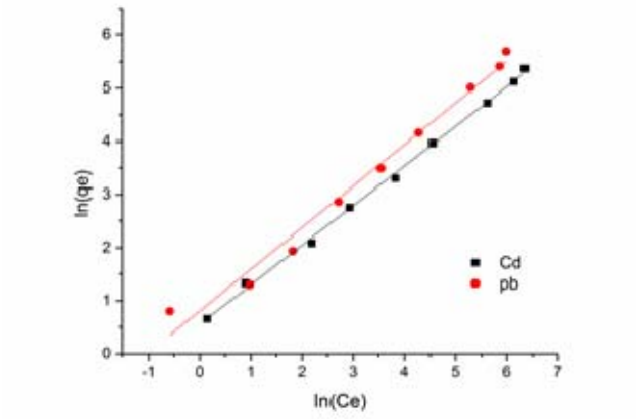

Fig. 7 Freundlich isotherm model for adsorption of Cd and Pb

According to the Figure 7, the high value of coefficient of determination (for Cd, R^2=0.9978 and for Pb, R^2=0.9820) obtained indicates a good agreement between the experimental values and isotherm parameters. Therefore, adsorptions of Cd and Pb in to chitosan are heterogeneous process and consider the interaction of adsorbed ions. The calculated n values for both Cd (n=1.34) and Pb (n=1.27) indicate the adsorption process is physical adsorption. Table 1 shows the isotherm constants and parameters

TABLE 1. Isotherm constants and regression data for adsorption of Cd and Pb

Adsorption isotherm	**metal**	**R^2**	**Isotherm Parameter**	
Langmuir	Cd	0.787	Q_m	234.47
			b	0.004
	Pb	0.6122	Q_m	387.59
			b	0.0034
Freundlich	Cd	0.9978	K_f	6.355
			n	1.34
	Pb	0.9820	K_f	3.560
			n	1.27

H. Adsorption kinetics study

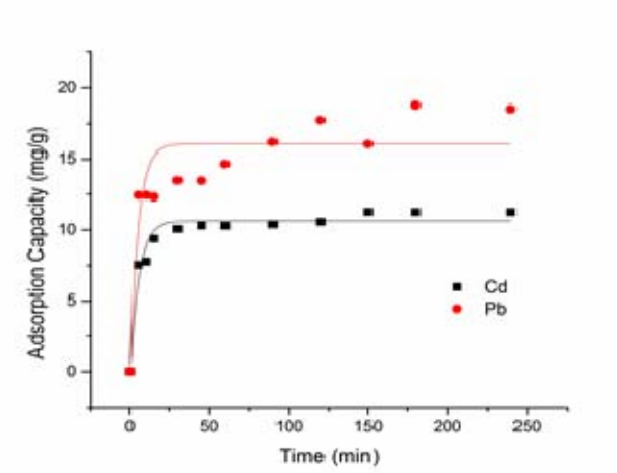

Fig. 8 Pseudo first order kinetics for Cd and Pb

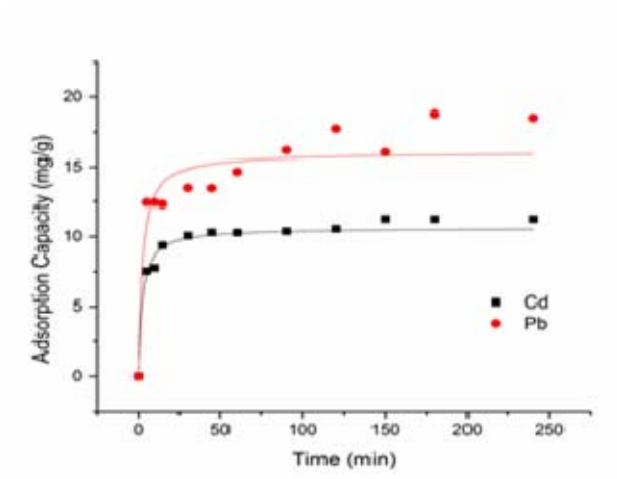

Fig. 9 Pseudo second order kinetics for Cd and Pb

The results shown in Figure 8 and Figure 9 reveal that Cd and Pb adsorption best can be described by a pseudo second order equation. The best correlation was observed for the low DD sample (R^2=0.988) and it was also good for the high DD sample (R^2=0.9852). As mentioned in the literature, pseudo first order equation did not fit the experimental data well [7]. According to the results shown in table 2, it can be clearly shown that pseudo second order model better fit with experimental data. Therefore pseudo second order adsorption mechanism is predominant and the overall rate of heavy metal ion adsorption is therefore controlled by adsorption reactions and not by mass transfer.

TABLE 2. Kinetic constants for adsorption of Cd and Pb

	q_e	Pseudo first order		Pseudo second order	
		K_1	R^2	K_2	R^2
Cd	10.6288	0.1810	0.9473	0.0402	0.9792
Pb	15.8018	0.2120	0.8264	0.0293	0.8780

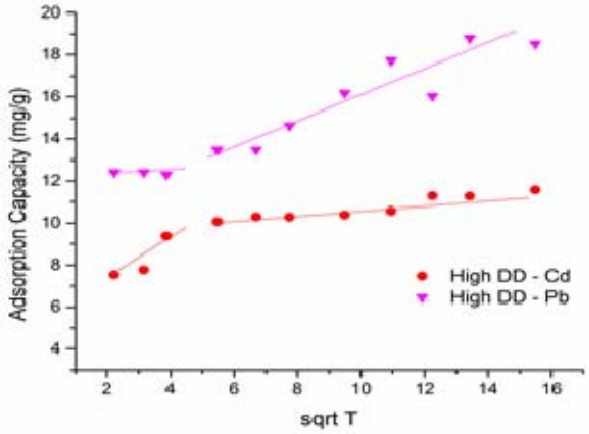

Fig 10. Intra-particle model of Cd and Pb adsorption

Figure 10 shows the intra-particle diffusion curve. The initial portion of the plot indicates the boundary layer effect while the other linear portion is due to the intra-particle or pore diffusion. The two phases in the plot suggest that the adsorption process facilitates by the surface adsorption and the intra-particle diffusion.

IV. Conclusions

DD value of the chitosan, initial pH of the metal ion solution and initial heavy metal concentration of the solution are the rate dependent parameters of the heavy metal adsorption. Significantly high percentage of adsorption was observed at high DD, high pH and low initial metal ion concentration. Effect of the particle size was not significant to the adsorption process with compare to the pH and DD variation. Therefore chemically modified chitosan (high DD) at higher pH value is suitable for the adsorption of Cd and Pb into chitosan. According to the isotherms models, adsorption of Cd and Pb ions into chitosan was fitted well with the Freundlich model and therefore it can be concluded that adsorption process is heterogeneous and facilitate multilayer adsorption. Pseudo second order model fitted well with experimental data and therefore sorption of Cd and Pb was controlled by the adsorption reaction and not from mass transfer. According to this study chitosan is a good candidate to remove heavy metals from wastewater especially at low concentrations (< 5ppm). Chitosan may offer an alternative to traditional adsorbent materials in wastewater treatment. The unique properties of chitosan together with availability make chitosan an exciting and promising agent for the heavy metal adsorption from wastewater.

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