



## Kinetics of cadmium adsorption by CNTs grown on PACs

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### Abstract

Isotherms and kinetic models are useful tool for the investigation of adsorption process. Carbon nanotubes (CNTs) grown on powdered activated carbons (PACs) was used as novel adsorbent. Two isotherms and three kinetic models were studied for the removal of cadmium from water. The isotherms were Langmuir and Freundlich and the kinetic models were pseudo first order, pseudo second order and intraparticle diffusion models. Langmuir constants were  $q_m = 69.759$  mg/g,  $K_1 = 0.223$  and  $R^2 = 0.924$ . The adsorption process was found more likely to follow Freundlich model with  $R^2$  value of 0.961,  $K_f$  of 9.215 and  $n$  of 3.015. Based on the kinetics study, the pseudo second order was the best fit with  $R^2$  of 0.996 and model constants were  $q_e = 34.29$  (mg/g) and  $K_2 = 0.0013$  (g/mg.min). Coefficients for the pseudo first order were  $q_e = 21.145$  (mg/g) and  $K_1 = 0.09$  ( $\text{min}^{-1}$ ) with  $R^2$  of 0.936. The intraparticle kinetic model exhibited  $R^2$  value of 0.812 with  $K_d = 1.295$  ( $\text{g/mg.min}^{0.5}$ ). CNTs after oxidative functionalization with  $\text{KMnO}_4$  were observed to be an efficient adsorbent for  $\text{Cd}^{2+}$  removal from water.

**Keywords:** Adsorption, cadmium, CNTs, kinetics, PACs.

### 1. Introduction

There has been a significant amount of research conducted for the advancement in many areas of nanotechnology such as, nanoparticles and powders, nanolayers and coats, electrical, optic and mechanical nanodevices, nanomedicine, nanosensors and nanostructured biological materials. Carbon nanotubes (CNTs) are the most favourable among other forms of nanomaterial. The most impressive features of these structures are their electronic, mechanical, optical and chemical characteristics, which open a way to various applications [1]. Several methods of (CNTs) production have been reported in the literature. The most common techniques used are, arc discharge, laser ablation and chemical vapour deposition. Chemical vapor deposition (CVD) is a versatile process suitable for the synthesis of various types of nanoproducts [2].

In the CVD-method different hydrocarbons such as benzene ( $\text{C}_6\text{H}_6$ ), pentane ( $\text{C}_5\text{H}_{12}$ ), acetylene ( $\text{C}_2\text{H}_2$ ), methane ( $\text{CH}_4$ ) and carbon monoxide is decomposed over different metallic catalysts (Fe, Co, Ni, etc.) at temperatures between 500 and 1200 °C. This

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method was used for a long time for the synthesis of carbon fibers and nanofiber [3, 4, 5] but there were no indications that it could also be used for the synthesis of carbon nanotubes until Yacamán *et al.*, [6] reported this method for the production of nanotubes. The CVD method deposits hydrocarbon molecules on top of heated catalyst material. Metal catalysts dissociate the hydrocarbon molecules. The CVD process uses hydrocarbons as the carbon source. Hydrocarbons flow through the quartz tube where it is heated at a high temperature [7]. The energy source is used to “crack” the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co). Carbon nanotubes will be formed if the proper parameters are maintained [8]. In CVD methods, the catalyst particle should be supported on a substrate such as silica, or alumina. The reported methods of catalyst support on the substrate are impregnation, deposition of catalyst particles on the substrate and sputtering [9]. In this research powdered activated carbon (PAC) was used as a new substrate to support the metallic catalyst (Fe) for the growth of CNTs. The new material was used in removing cadmium from water. Two isotherms and three kinetic models were studied for the removal of cadmium from water. The isotherms were Langmuir and Freundlich and the kinetic models were pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

## 2. Methodology

### 2.1 Production of Adsorbent

Powdered activated carbon (PAC) having particle size between 100 and 250  $\mu\text{m}$  was impregnated with  $\text{Fe}^{3+}$  catalyst. The source of  $\text{Fe}^{3+}$  catalyst was iron nitrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , which was dissolved in acetone. The two elements were mixed together in a 2 cm Dia glass bottles and placed in a sonication bath for 1 hour. Then the temperature of the sonication bath was raised to 60  $^\circ\text{C}$ . The mixture was dried under ultrasonic condition until all the solvents were evaporated. The dried cake was grinded. The catalyst-support powder was subjected to two heat treatment steps. At first the impregnated PACs were calcinated in  $\text{N}_2$  filled atmosphere at 350  $^\circ\text{C}$  for 1 hour. Then those were reduced by  $\text{H}_2$  at 350  $^\circ\text{C}$  for 1 hour. Both of these processes are carried out in a CVD tubular ceramic tube reactor (50 mm OD, 40 mm ID, 1500 mm L). Heat treated impregnated PACs were placed in a ceramic boat inside the CVD reactor and heated to the growth temperature (650  $^\circ\text{C}$ ) in an atmosphere filled with  $\text{N}_2$  gas. Then the  $\text{N}_2$  flow was stopped and the reaction gases  $\text{H}_2$  (300 ml/min) +  $\text{C}_2\text{H}_2$  (50 ml/min) were inserted for different contact time (30 min to 90 min). After that the reactor was cooled down to room temperature in presence of  $\text{N}_2$  gas.

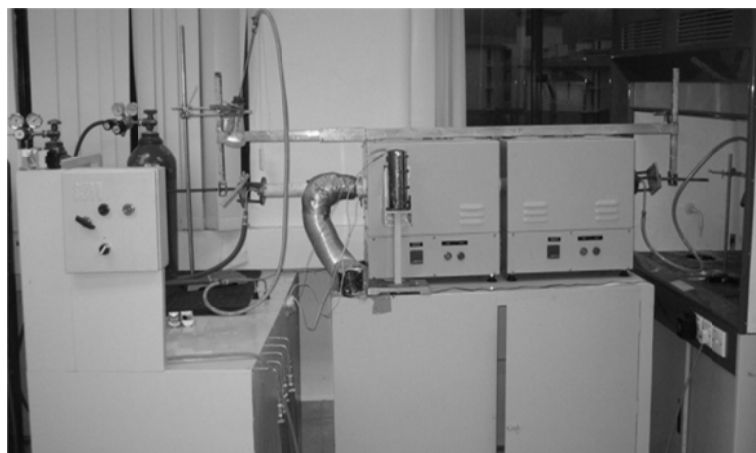


Fig. 1: The CVD reactor.

## 2.2 Adsorption Isotherm

Various initial concentrations of  $\text{Cd}^{2+}$  (2.5, 6.0, 9.0, 14.0, 18.0 and 35.0 mg/L) were employed to perform adsorption equilibrium isotherm experiments. The adsorption runs were conducted at conditions of pH 5.5, dose of CNT-PAC 200 mg/L, agitation speed 180 rpm and various time intervals (10, 30, 120 and 600 min). Aqueous solution of  $\text{Cd}^{2+}$  was prepared and pH was maintained close to 5.5. Then 10 mg of CNT-PAC adsorbent was added into 50 ml volume of solution in a 100 ml conical flask and fixed on the shaker which was operated at speed 180 rpm for the selected time intervals. The solution was filtered using Whatman filter paper no. 131. The  $\text{Cd}^{2+}$  concentration of the filtrate solution was measured using Perkin Elmer 300 AAS, USA. The concentration was plotted against time to get the equilibrium concentration.

To apply the different adsorption isotherm models, adsorption capacity  $q$  (mg/g) was calculated using the following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where  $q_t$  and  $q_e$  are the adsorption capacity (mg/g) at time  $t$  and at equilibrium after long period of time,  $C_0$ ,  $C_t$  and  $C_e$  are initial concentration and concentration of  $\text{Cd}^{2+}$  at time  $t$  (min) and equilibrium time respectively,  $V$  is the volume of solution (ml) and  $m$  is the amount of adsorbent (g).

## 2.3 Adsorption Kinetics

Three kinetics models were used to investigate the kinetics of the adsorption system of ( $\text{Cd}^{2+}$ ) in aqueous solution for the novel CNT-PAC as adsorbent. The models used in this research were, i) pseudo first order, ii) pseudo second order and iii) intraparticle diffusion model [10, 11, 12].

### 3. Results and Discussion

Findings of the adsorption isotherm studies (Freundlich and Langmuir) and three different adsorption kinetic models (pseudo-first order, pseudo-second order and intraparticle) are reported in this section.

#### 3.1 Adsorption Isotherms

In this study, the equilibrium uptake concentration ( $q_e$ ) of cadmium on solid phase adsorbent was directly proportional to  $Cd^{2+}$  concentration in liquid phase, which can be attributed to saturation of the adsorption sites or layers through the adsorption process. Such observation was also reported by many researchers in the field of sorption processes [13, 14, 15, 16, 17].

Fig. 2 shows the values of  $\ln(q_e)$  plotted versus  $\ln(C_e)$ . It was observed that the isotherm data fitted Freundlich linear form model resulting in a correlation coefficient value ( $R^2$ ) of 0.9612. Values of  $K_f$  and  $n$  were determined from the intercept and slope of the line to be 19.215 and 3.015, respectively.

The adsorption data were fitted with the linearized Langmuir model as shown in Fig. 3 that resulted in correlation coefficient ( $R^2$ ) value of 0.9242. The values of  $K_L$  and  $q_m$  were determined from the plot (Fig. 3) and were found to be 0.223 (L/mg) and 69.759 (mg/g), respectively.

The values of correlation coefficients indicated that the adsorption of  $Cd^{2+}$  was well fitted with Freundlich while its fitness with Langmuir was inferior to that of Freundlich model. Similar observation has been reported by several researchers in removal of nickel from water by multi wall CNTs and removal of cadmium using as grown CNTs, oxidized CNTs, activated carbon and fly ash [19, 20, 21, 22].

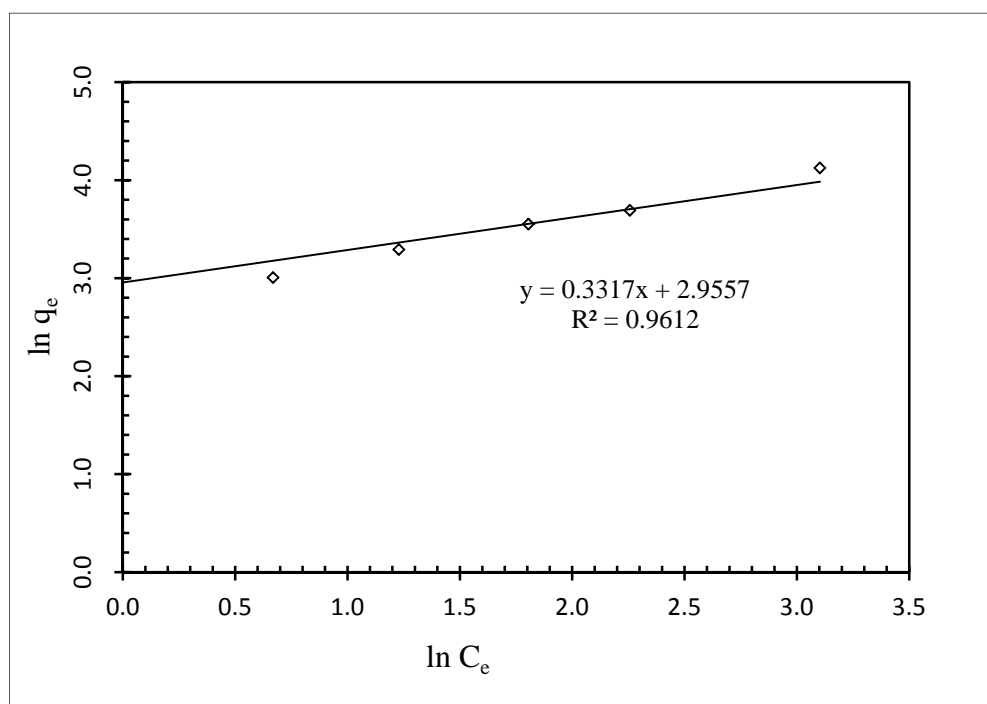


Fig. 2: Freundlich linear form for  $Cd^{2+}$  adsorption on CNT-PAC in water.

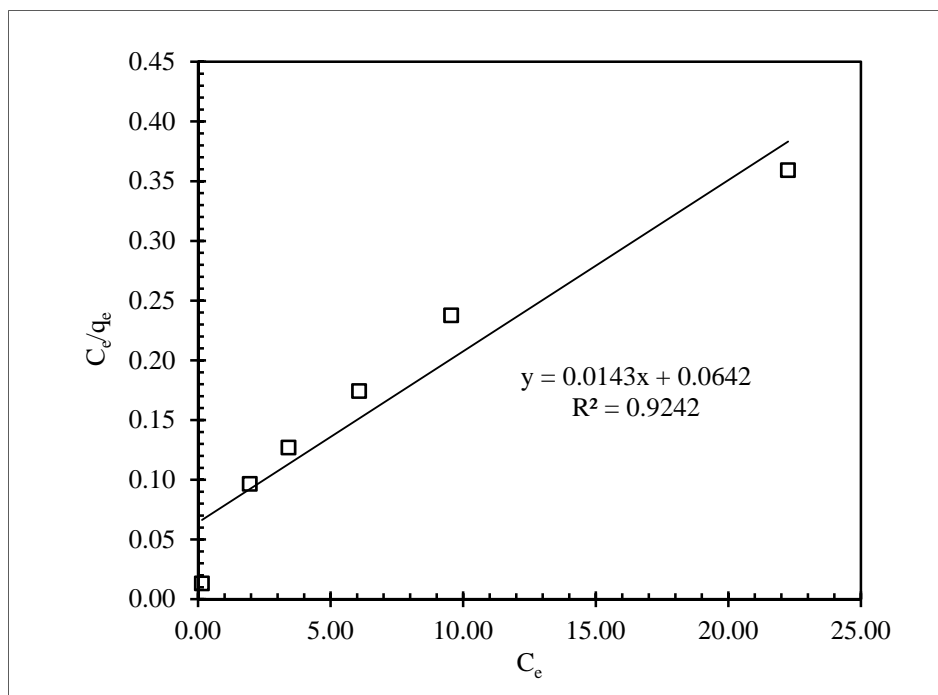


Fig. 3: Langmuir isotherm linear form for Cd<sup>2+</sup> adsorption on CNT-PAC in water.

Freundlich and Langmuir constants have been reported for various adsorbent used for removal of heavy metals by several researchers. These constants values in some of these works are compared with the Freundlich and Langmuir constants obtained in the present work as shown in Table 1. It can be observed that the isotherm parameters for the CNT-PAC adsorbent synthesized in the present study had high values comparing to other types of adsorbents as given in the Table 1. Such observation indicates the good performance of the CNT-PAC as an adsorbent for cadmium removal from water.

Table 1: Adsorption isotherm models for CNT-PAC comparing with different adsorbents

Adsorption Isotherm Model		Langmuir			Freundlich		Reference	
Adsorbent	Adsorbate	$q_m$ (mg/g)	$K_L$ (l/mg)	$R^2$	$n$	$K_f$ (mg/g)	$R^2$	
CNT-PAC	Cd <sup>2+</sup>	69.759	0.2230	0.924	3.015	19.215	0.961	Present work
Bagasse Fly Ash	Cd <sup>2+</sup>	6.1942	0.0899	0.985	0.469	0.8544	0.999	[20]
Activated Carbon	Cd <sup>2+</sup>	19.590	0.4800	0.958	4.280	8.3200	0.991	[21]

### 3.2 Adsorption Kinetics

After plotting the sets of data, the values of correlation coefficient  $R^2$  were considered as indications of conformity between experimental data and the corresponding values predicted by each model. Relatively high  $R^2$  (equal to or close to 1) indicated that the model described the process successfully. Fig. 4 shows the plot of  $\ln(q_e - q_t)$  against time representing the linear form of pseudo first order kinetic model. The rate constant  $K_1$  was calculated from the slope of the straight line obtained.  $K_2$  was the rate constant of pseudo second order adsorption kinetics (g/mg.min) was calculated from the intercept and slope of the straight line of  $t/q_t$  against time,  $t$  (Fig. 5). The rate constant of intraparticle diffusion,  $K_d$  is (g/mg.min<sup>0.5</sup>) calculated from the slope of plot  $qt$  against  $t^{0.5}$ , as shown in Fig. 6.

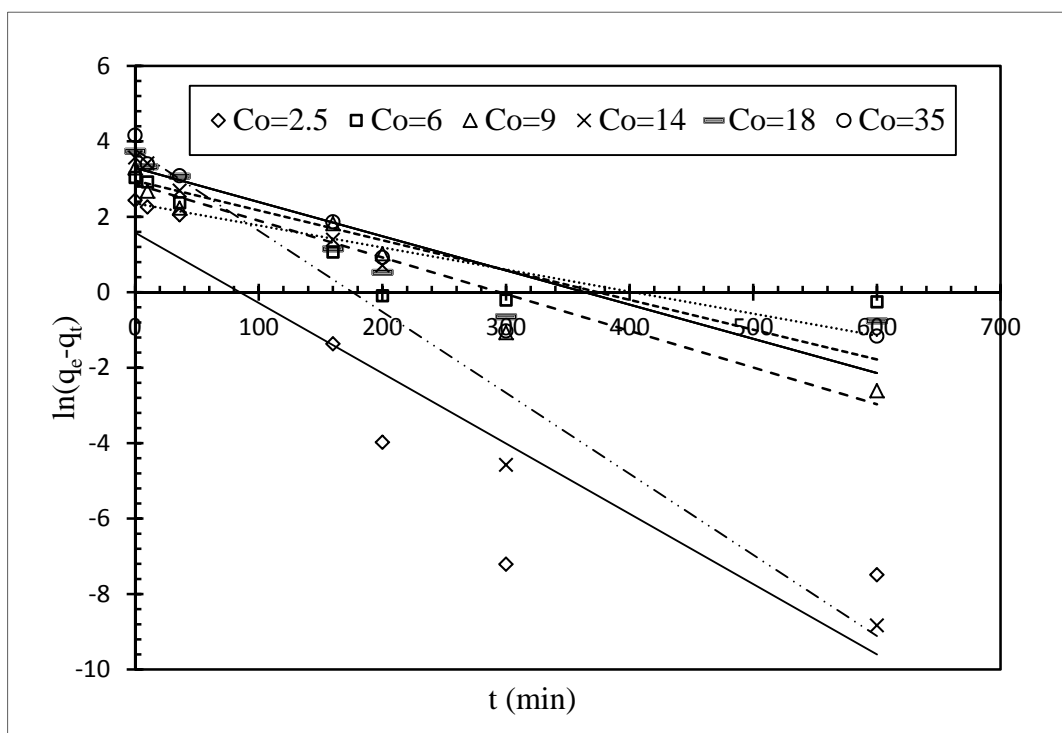


Fig. 4: Pseudo first order adsorption kinetics at different initial concentrations, the initial concentration in (mg/L).

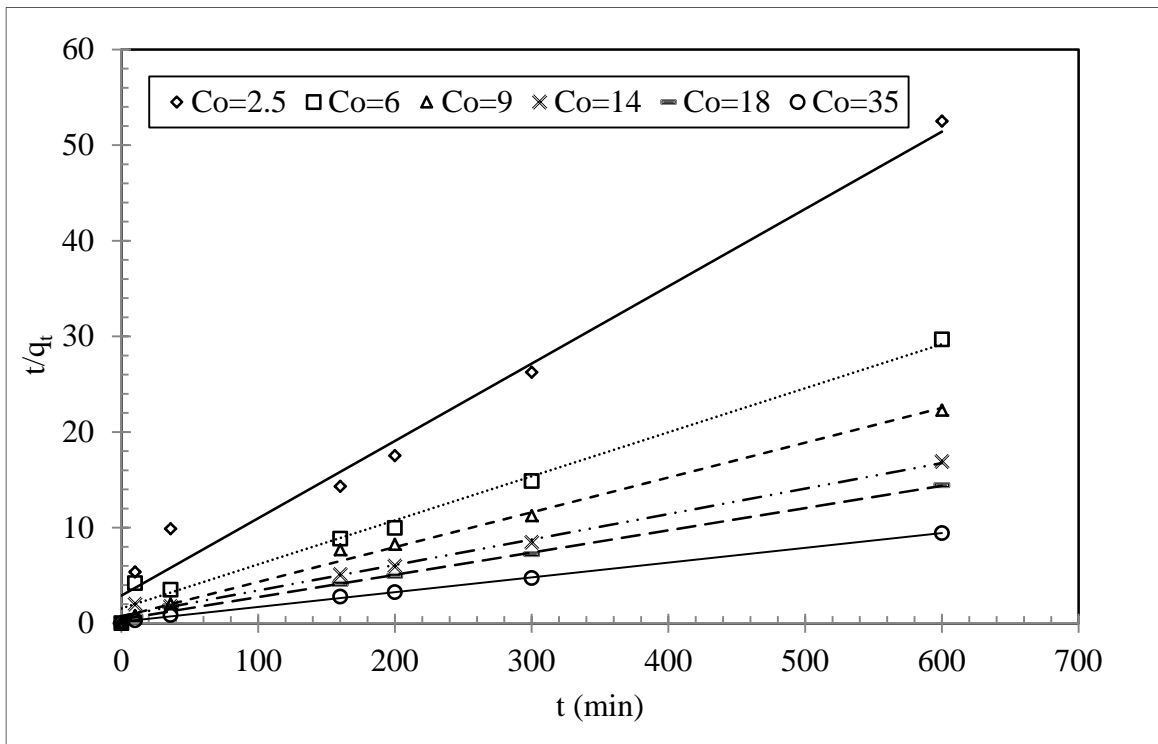


Fig. 5: Pseudo second order adsorption kinetics at different initial concentrations, the initial concentration in (mg/L).

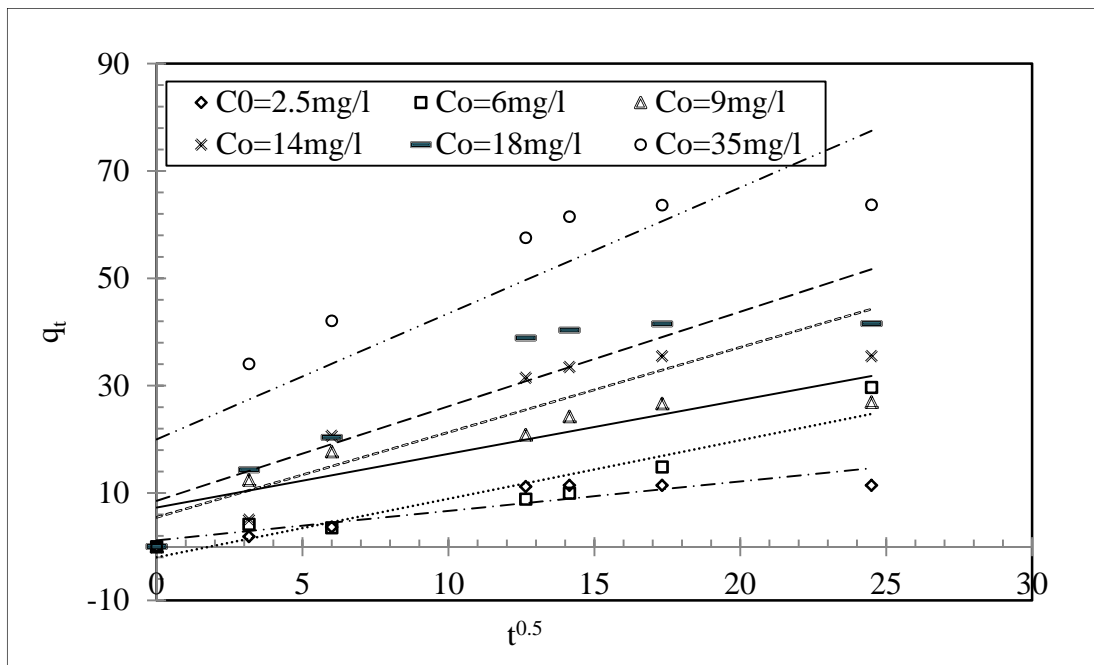


Fig. 6: Intraparticle adsorption kinetics at different initial concentrations, the initial concentration in (mg/L).

Comparison of different correlation coefficients ( $R^2$ ) obtained by applying different kinetic models on the same set of data at various concentrations are given in Table 2. The kinetics of adsorption of  $Cd^{2+}$  ions adsorption on CNT-PAC followed the pseudo second order with more conformity comparing with pseudo first order and intraparticle models since the  $R^2$  of the pseudo second order was varying from 0.989 to 0.999 with average of 0.996. While in the case of pseudo first order average  $R^2$  was in the range from 0.936 and 0.812 in case of intraparticle kinetics model. Based on that observation it can be claimed that the adsorption reaction of  $Cd^{2+}$  cations on CNT-PAC is quantitatively described by pseudo-second-order kinetics model. The pseudo second order rate has been applied widely to the sorption of metal ions, herbicides, oils and organic substances from aqueous systems [23]. When intraparticle transport (pore diffusion) is the rate-limiting step, a functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half-power of time,  $t^{0.5}$ , rather than  $t$ ; nearly linear variation of the quantity adsorbed with  $t^{0.5}$  is predicted for a large initial fraction of reactions controlled by rates of intraparticle diffusion [23, 24].

Table 2: Experimental values of constants of adsorption kinetic models

$C_0$ (mg/L)	Pseudo-first- order			Pseudo-second-order			Intraparticle	
	$q_e$ (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ (mg/g)	$K_2$ (g/mg.min)	$R^2$	$K_d$ (g/mg.min <sup>0.5</sup> )	$R^2$
2.5	9.573	0.502	0.983	12.714	0.0013	0.989	0.8974	0.973
6	14.480	0.005	0.889	22.290	0.0008	0.994	0.8517	0.835
9	19.383	0.009	0.981	27.828	0.0013	0.995	0.9207	0.773
14	25.322	0.009	0.978	37.604	0.0006	0.996	1.4321	0.802
18	22.199	0.006	0.799	41.979	0.0010	0.998	1.5660	0.798
35	35.912	0.011	0.986	63.328	0.0011	0.999	2.1047	0.689

Fig. 6 showed plots of the amount of  $Cd^{2+}$  per unit weight of CNT-PAC against the square root of  $t$ . The poor linearization ( $R^2 < 0.9$ ) of the data was observed (Table 2) for the initial phase of the reaction in accordance with the expected behavior if intraparticle diffusion is not the rate-limiting step for the whole adsorption process. Straight lines could be obtained at the very beginning. Similar sorption phenomena have also been reported by Ho et al. [23]. However, it did not pass through the origin which indicates intraparticle diffusion might not be the rate limiting step.

#### 4. Conclusion

This study was conducted to test the fitting of adsorption data to the Freundlich and Langmuir isotherms and three kinetic models namely, pseudo first order, pseudo second order and intraparticle diffusion model. With respect to the  $R^2$  values, the adsorption process was found more likely to follow the Freundlich model. The present study also revealed that the CNT-PAC adsorption system followed the pseudo second order kinetics in removing  $Cd^{2+}$  from aqueous solution.



## Acknowledgments

This project was funded by the fundamental research grant scheme (FRGS - 0106-42) administered by the ministry of higher education, Government of Malaysia.

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