Kinetics of Cadmium Adsorption by CNTs Grown on PACs

Abdullah Al Mamun[1], Mohammed A. Al-Saadi[1], Suleyman A. Muyibi[1], Md. Zahangir Alam[1], Iis Sopyan[2]

[1] Nanoscience and Nanotechnology Research Group (NANORG), Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia
[2] Department of Manufacturing and Material Engineering, Faculty of Engineering, International Islamic University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia

E-mail: (mamun@iium.edu.my)

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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_l = 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 (min^{-1}) with R^2 of 0.936. The intraparticle kinetic model exhibited R^2 value of 0.812 with K_d = 1.295 (g/mg.min$^{0.5}$). CNTs after oxidative functionalization with $KMnO_4$ were observed to be an efficient adsorbent for Cd^{2+} removal from water.

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 (C_6H_6), pentane (C_5H_{12}), acetylene (C_2H_2), methane (CH_4) and carbon monoxide is decomposed over different metallic catalysts (Fe, Co, Ni, etc.) at temperatures between 500 and 1200 °C. This 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.

Methodology

Production of Adsorbent. Powdered activated carbon (PAC) having particle size between 100 and 250 μm was impregnated with Fe^{3+} catalyst. The source of Fe^{3+} catalyst was iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$, 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 hr. Then the temperature of the sonication bath was raised to 60 ^{o}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 N_2 filled atmosphere at 350 ^{o}C for 1 hr.   Then those were reduced by H_2 at 350 ^{o}C for 1 hr. 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 ^{o}C) in an atmosphere filled with N_2 gas. Then the N_2 flow was stopped and the reaction gases H_2 (300 ml/min) + C_2H_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 N_2 gas.

Figure 1: The CVD reactor

Adsorption Isotherm. Various initial concentrations of 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 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 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:

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

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (2)$$

where q_t and q_e are the adsorption capacity (mg/g) at time t and at equilibrium after long period of time, C_o, C_t and C_e are initial concentration and concentration of 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).

Adsorption Kinetics. Three kinetics models were used to investigate the kinetics of the adsorption system of (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].

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.

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 stauration 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].
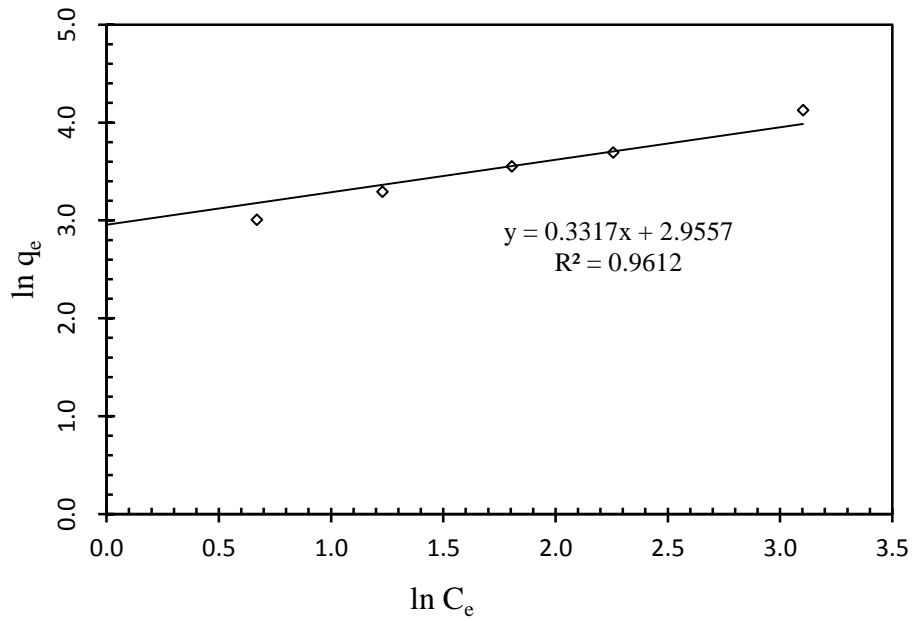
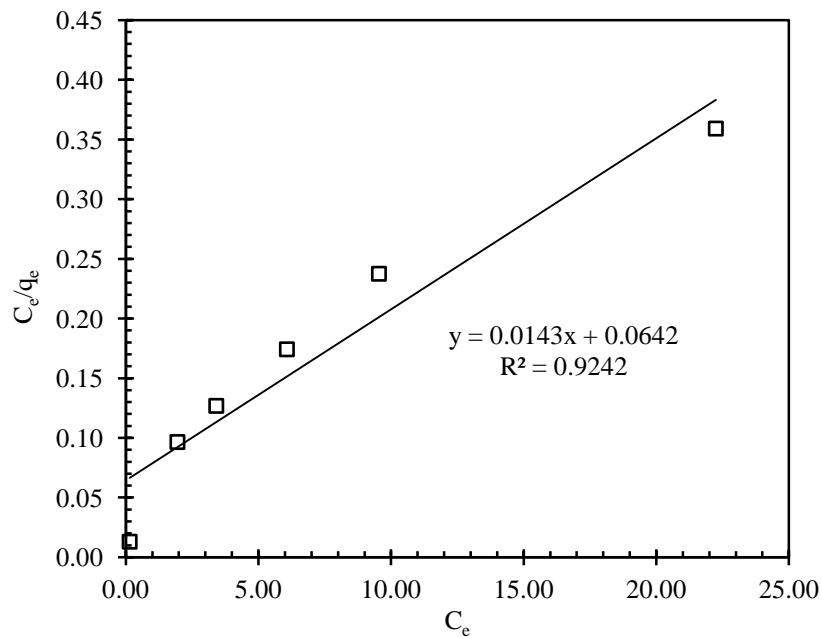Figure 2: Freundlich linear form for Cd^{2+} adsorption on CNT-PAC in water

Figure 3: Langmuir isotherm linear form for Cd^{2+} 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^{2+}	69.759	0.2230	0.924	3.015	19.215	0.961	Present work
Bagasse Fly Ash	Cd^{2+}	6.1942	0.0899	0.985	0.469	0.8544	0.999	[20]
Activated Carbon	Cd^{2+}	19.590	0.4800	0.958	4.280	8.3200	0.991	[21]

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$^{0.5}$) calculated from the slope of plot qt against $t^{0.5}$, as shown in Fig. 6.
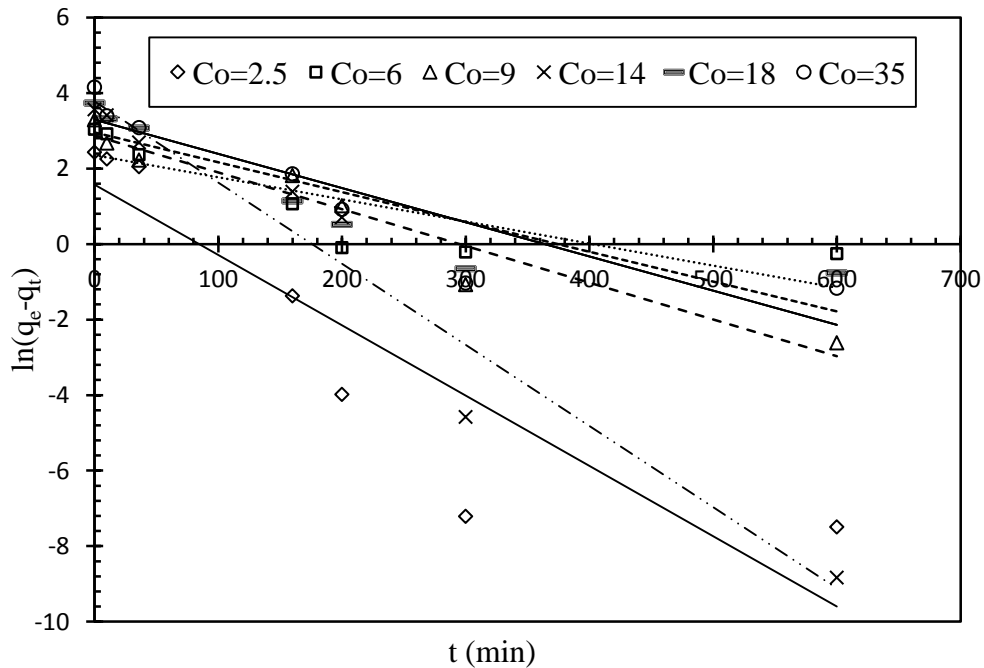

Figure 4: Pseudo first order adsorption kinetics at different initial concentrations, the initial concentration in (mg/L)
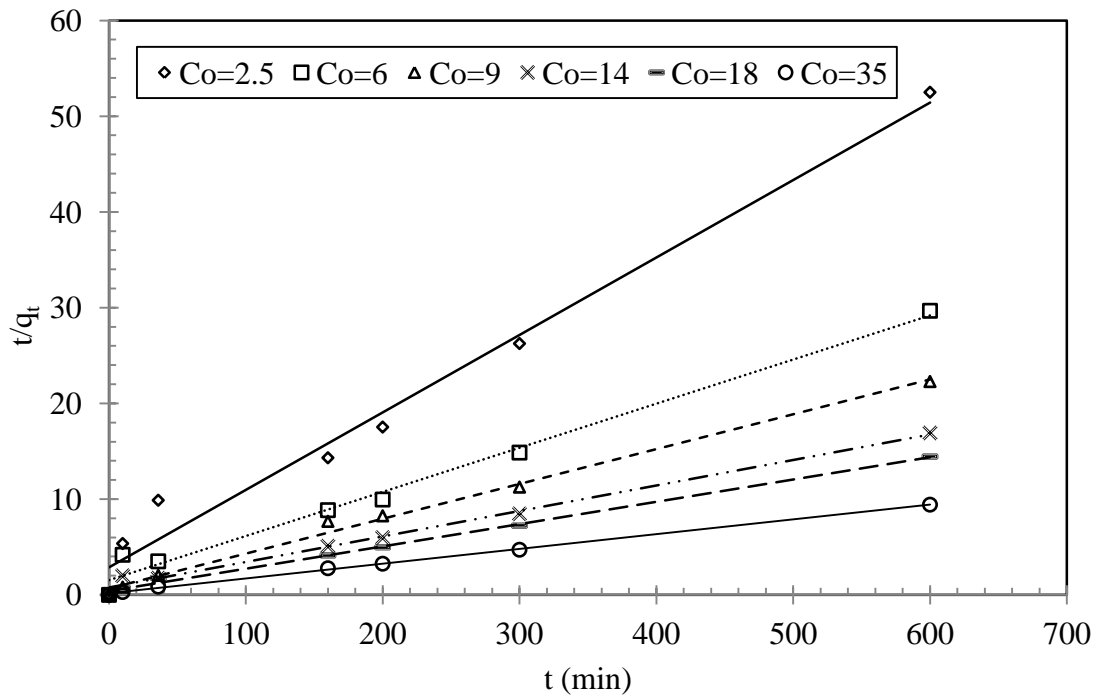
Figure 5: Pseudo second order adsorption kinetics at different initial concentrations, the initial concentration in (mg/L)
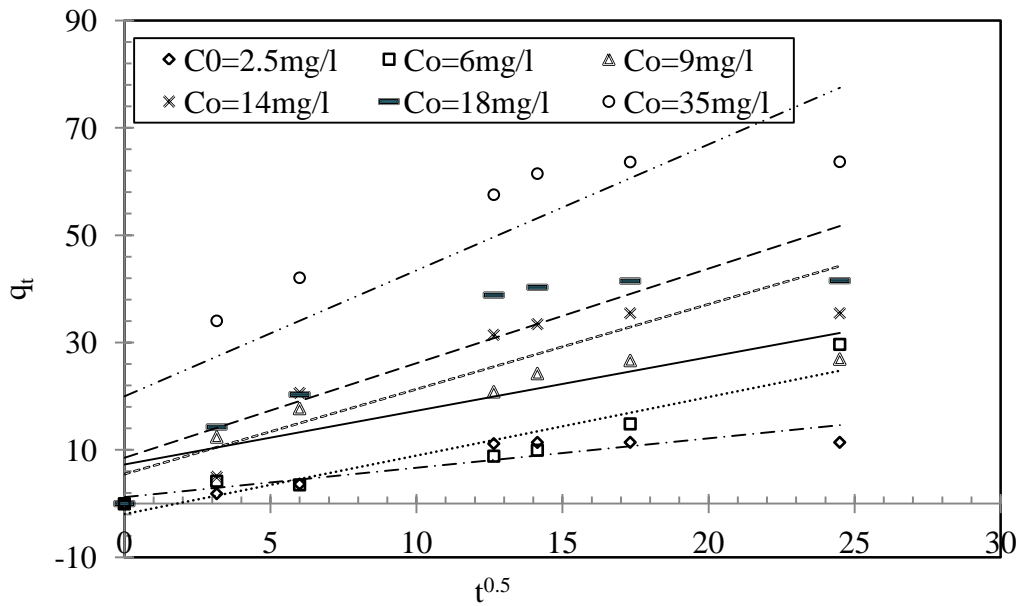

Figure 6: Intraparticle adsorption kinetics at different initial concentrations, the initial concentration in (mg/L)

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 psuedo 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_o (mg/L)	Pseudo-first- order			Pseudo-second-order			Intraparticle	
	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg.min)	R^2	K_d (g/mg.min$^{0.5}$)	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.

Conclusions

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.

Acknowledgment

References

[1] M. Dresselhaus, G. Dresselhaus, P. Avouris, Carbon nanotubes: synthesis, structure, properties, and applications, Springer Verlag, Berlin, 2001.

[2] H.O. Pierson, Handbook of chemical vapor deposition (CVD) principles, Technology, and Applications (2nd ed.), New York, USA, William Andrew publishing, llc Norwich, 1999.

[3] Y.Y. Li, S.D. Bae, A. Sakoda, M. Suzuki, Formation of vapor grown carbon fibers with sulfuric catalyst precursors and nitrogen as carrier gas, Carbon. 39(2001), 91–100.

[4] J.L. Cheol, C. Seung K. Hyoun-Woo, P. Chong-Yun, Y. Cheol-Woong, Large-scale production of aligned carbon nanotubes by the vapor phase growth method, Chemical Physics Letters. 359(2002),109–114.

[5] L.F. Sun, Z.Q. Liu, X.C. Ma, D.S. Tang, W.Y. Zhou, X.P. Zou, Y.B. Li, Y.J. Lin, J.Y. Tan, S.S. Xie, Growth of carbon nanofibers array under magnetic force by chemical vapor deposition, Chemical Physics Letters. 336(2001), 392–396.

[6] M.J. Yacaman, M.M. Yoshida, L. Rendon, Catalytic growth of carbon microtubles with fullerene structure, Appl Phys Lett. 62(1993), 202–204.

[7] S.B. Sinnot, R. Andrews, D. Qian, A. M. Rao, Z. Mao, E. C., Dickey, F. Derbyshire, Model of carbon nanotube growth through chemical vapor deposition, Chemical Physics Letters. 315(1999), 25-30.

[8] Z.F. Ren, Z. P. Huang, D. Z. Wang, J. G. Wen, J. W. Xu, J. H. Wang, L. E. Calvet, J. Chen, J. F. Klemic, M. A. Reed, Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot, Applied Physics Letters. 75(1999), 8-10.

[9] K. Jing, T. S. Hyongsok, M. C. Alan, F. Q. Calvin, D. Hongjie, Synthesis of individual singlewalled carbon nanotubes on patterned siliconwafers, Nature. 395(1998).

[10] Y. Ho, Review of second-order models for adsorption systems, Journal of hazardous materials 136(2006), 681-689.

[11] M. Wright, An introduction to chemical kinetics, Wiley Online Library, 2004.

[12] V. Vilar, C. Botelho, R. Boaventura, Equilibrium and kinetic modelling of Cd (II) biosorption by algae Gelidium and agar extraction algal waste, Water Research. 40(2006), 291-302.

[13] M. Achak, A. Hafidi, N. Ouazzani, S. Sayadi, L. Mandi, Low cost biosorbent, Journal of hazardous materials. 166(2009), 117-125.

[14] E. Pehlivan, S. Cetin, B. Yanik, Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash, Journal of hazardous materials. 135(2006), 193-199.

[15] V.C. Srivastava, I.D. Mall, I.M. Mishra, Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash, Chemical Engineering Journal. 117(2006), 79-91.

[16] V. Vilar, C. Botelho, R. Boaventura, Equilibrium and kinetic modelling of Cd (II) biosorption by algae Gelidium and agar extraction algal waste, Water Research. 40(2006), 291-302.

[17] Y. Jia, K. Thomas, Adsorption of cadmium ions on oxygen surface sites in activated carbon, Langmuir. 16(2000), 1114-1122.

[18] T. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Research. 37(2003), 4311-4330.

[19] M. Kandah, J. Meunier, Removal of nickel ions from water by multi-walled carbon nanotubes, Journal of hazardous materials. 146(2007), 283-288.

[20] R.M. Madhava, A. Ramesh, P.C. Rao, K. Seshaiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls, Journal of hazardous materials. 129(2006), 123-129.

[21] V.C. Srivastava, I.D. Mall, I.M. Mishra, Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash, Chemical Engineering Journal. 117(2006), 79-91.

[22] Y. Ho, D. Wase, C. Forster, C. Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, Environmental Technology. 17(1996), 71-77.

[23] Y. Ho, A. Ofomaja, Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution, Process Biochemistry. 40(2005), 3455-3461.

[24] J. Weber, J.Morris, Kinetics of adsorption on carbon from solution. J Sanit Eng Div ASCE. 89(1963), 28.