Kinetic study of adsorption of NH_3 gas on pristine and tin oxide functionalised Carbon Nanotubes

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Abstract

Carbon nanotube gas sensors in its pristine and functionalized form have been studied in detail to sense environment polluting gases. The current work aims to study the kinetics of adsorption of ammonia gas by pristine and SnO_2 functionalized single walled carbon nanotubes. The functionalization is done by 0.1 mg, 0.2 mg and 1mg SnO_2. The observed response in the form of change in conductivity is studied using Boyd model, interparticle diffusion model and Weber and Morris model. The adsorption process is mainly governed by intraparticle diffusion. The optimum value of rate constant obtained for 0.1 mg SnO_2 points to the limited use of SnO_2 for functionalization.

Keywords: Ammonia, Boyd model, interparticle diffusion model, Weber and Morris model

Introduction:

Ammonia (NH_3) is the most common by-product of many industrial and agricultural activities. Inhalation of a small amount of NH_3 causes coughing and leads to throat and nose irritation. Even low concentration of ammonia present in air may produce eye irritation and skin rashes. Annihilation of this gas for a long time can cause adverse effects on the health of young children [1]. Carbon nanotubes due to their exceptional physical and electronic properties are widely used as gas sensors for NH_3 gas [2]. Work has been previously reported for sensing ammonia gas by single walled carbon nanotubes (SWNT) and multi walled carbon nanotubes (MWNT) [3,4]

SWNT gas sensors show a response to NH_3 gas, however its pristine form suffers challenges like low responsivity and high recovery time at room temperature [5]. An improvement in responsivity is observed on functionalization of SWNT with metal oxides [6]. Tin Oxide (SnO_2) functionalized SWNT shows an increase in responsivity as compared to pristine when exposed to ammonia gas [7]. Rate kinetic models and isotherm studies give a deep understanding of the adsorption phenomenon and may help in designing effective gas sensors. The study on adsorption mechanism of pristine SWNT and SnO_2 functionalized SWNT for NH_3 gas using various isotherm models is reported earlier [6]. Adsorption kinetics of ammonium ions by MWNTs using various models is reported [8].

Objectives of the paper

In the present study, rate kinetics of 0.1mg, 0.2 mg and 1mg SnO_2 functionalized SWNT are analysed using various rate kinetic models for adsorption of ammonia gas.

Methodology/ Experimental

Powder of pristine SWNT was purchased from carbon solutions [7]. Tin oxide nanoparticles obtained by the reduction of $SnCl_2.2H_2O$ using NH_3 solution were used to functionalize SWNTs dispersed in dimethylformamide solution with 0.1mg, 0.2mg and 1mg tin oxide particles. The samples obtained after vacuum filtration and baking at 75°C were characterized by X ray diffraction and Scanning electron microscopy [7]. After annealing the gas sensors at 400°C in presence of nitrogen, they were mounted on a PCB header and kept in a closed gas chamber. They were then exposed to different concentrations of NH_3 gas. The sensor response is measured in terms of change in resistance using highly sensitive Fluke 289 multimeter at 23°C and ~40-48% relative humidity. The experimental procedure and set up was reported in detail earlier [7].

TABLES

Table 1: Estimated values of $\Delta\sigma_e$ using pseudo second order model

Concentration of gas		20ppm	8 ppm	2 ppm
Pristine SWNT	$\Delta\sigma_e$	0.2256	0.1521	0.0851

	R^2	*0.9896*	*0.9893*	*0.9793*
Functionalized SWNT with SnO_2				
0.1mg	$\Delta\sigma_e$	0.4535	0.286	0.1426
	R^2	*0.9852*	*0.9773*	*0.9617*
0.2mg	$\Delta\sigma_e$	0.3909	0.2711	0.1797
	R^2	*0.9799*	*0.9775*	*0.9145*
1mg	$\Delta\sigma_e$	0.1809	0.1522	0.0765
	R^2	*0.9797*	*0.9758*	*0.9538*

Table 2: Values of intercepts for inter particle diffusion model

Concentration of gas		20 ppm	8 ppm	2 ppm
Pristine SWNT	**C**	0.4176	0.4328	0.3065
	R^2	*0.9873*	*0.9851*	*0.9921*
Functionalized SWNT with SnO_2				
0.1mg	**C**	0.2918	0.2346	0.1414
	R^2	*0.9909*	*0.9927*	*0.991*
0.2mg	**C**	0.1997	0.1488	0.0371
	R^2	*0.9963*	*0.9878*	*0.9847*
1mg	**C**	0.3274	0.2977	0.1459
	R^2	*0.9851*	*0.9844*	*0.9904*

Table 3: The values of intraparticle rate constant for Weber and Morris model

Concentration of gas		20ppm	8 ppm	2 ppm
Pristine SWNT	**K_{ipd}**	0.0198	0.0132	0.0081
	R^2	*0.9694*	*0.9784*	*0.998*
Functionalized SWNT with SnO_2				
0.1mg	**K_{ipd}**	0.0431	0.0281	0.014
	R^2	*0.9861*	*0.9922*	*0.9987*
0.2mg	**K_{ipd}**	0.0394	0.0277	0.0129
	R^2	*0.996*	*0.9846*	*0.9955*
1mg	**K_{ipd}**	0.0165	0.014	0.0078
	R^2	*0.9958*	*0.9954*	*0.9964*

$\Delta\sigma_e$ is change in conductivity at equilibrium, C is the Y intercept of graph plotted between ln (1-F(t)) vs t where F(t) is a factor which determines the fractional attainment of equilibrium and t is the time, K_{ipd} is the rate kinetic constant for intraparticle diffusion.

Results

The X ray diffraction pattern taken using source of Cu-K_α beam (1.54 Å) confirms the formation of SnO_2 nano particles (Figure 1) and Scanning electron microscopy (Ziess-SUPRA-55) is seen to gives the good adherence of tin oxide nano particles [7] on SWNTs (Figure 2).

Kinetic study

Adsorption kinetics gives the information about the mechanism of uptake of adsorbate in the absorption process.

Lagergren pseudo first order model (PFO) proposes the kinetics of diffusion process

through a boundary. It is given by equation [9]

$$log\left(1-\frac{q_t}{q_e}\right)=\frac{K_1}{2.303}t \quad \text{-------(1)}$$

Where K_1 is rate constant, q_t is quantity adsorbed in time t and q_e is quantity adsorbed at equilibrium. Exposure to electron donating NH_3 gas on pristine and SnO_2 functionalized SWNT causes increase in resistance [5]. The change in conductivity is calculated for samples of dimensions 4mm × 1.5mm × 50μm. The observed conductivity change can be taken proportional to the charge using Drude's relation which will be proportional to quantity of gas adsorbed on the sensor [6]. Hence q_t and q_e are replaced by $\Delta\sigma_t$ and $\Delta\sigma_e$ respectively.

The equation for pseudo first order model in terms of change in conductivity can be modified as

$$log\left(1-\frac{\Delta\sigma_t}{\Delta\sigma_e}\right)=\frac{K_1}{2.303}t \quad \text{---------- (2)}$$

Pseudo first order model has not been considered here as gas is exposed for a fixed time of 60 sec and $\Delta\sigma_e$ can be estimated only by pseudo second order model.

Pseudo second order model (PSO) describes kinetics of adsorption process by chemisorption at the surface [10]. It is given by the equation [11].

$$\frac{t}{\Delta\sigma_t}=\frac{1}{K_2\,\Delta\sigma_e{}^2}+\frac{t}{\Delta\sigma_e} \quad \text{----------(3)}$$

K_2 is second order rate constant. This model is used to estimate the value of $\Delta\sigma_e$.

The graphs of $\frac{t}{\Delta\sigma_t}$ vs t for pristine and SnO_2 functionalized SWNT are shown in figure 3. The estimated values of $\Delta\sigma_e$ are reported in table 1 and further used to describe diffusion models. The values show an increase with increase in concentration of gas. Optimum values are obtained for 0.1 mg functionalized SWNTs.

In the process of adsorption of a gas on a solid adsorbent, mass transfer takes place from gaseous phase to solid phase. This process may be physisorption or chemisorption. There are many mass transfer mechanisms which depend upon the adsorbent morphology. However, mechanism based on diffusion can be considered more appropriately to describe adsorption of gases on solids. The adsorption of a gas on solid adsorbent usually takes place in different steps i.e., 1. Bulk diffusion, 2. Film diffusion, 3. Interparticle diffusion, 4. Surface diffusion, 5. Intraparticle diffusion [12]. As the bulk diffusion and surface diffusion are rapid hence their contribution is considered insignificant in comparison to other processes.

Boyd film diffusion model

Film diffusion is the process in which adsorbate (NH_3) is transported within the pores of the adsorbate. Boyd model for film diffusion is expressed by equation [13].

$$B(t)=-ln\frac{\pi^2}{6}-ln\,(1-F(t)) \text{ for } F(t)>0.85 \quad \text{---------- (4)}$$

$$B(t) = \{\sqrt{\pi} - \sqrt{\frac{\pi^2}{3} F(t)}\}^2 \quad \text{for } F(t) \leq 0.85$$

---------- (5)

Where $F(t)$ is a factor which determines the fractional attainment of equilibrium.

$F(t) = \frac{\Delta\sigma_t}{\Delta\sigma_e}$

And $B(t)$ is Boyd number. In the present studies the estimated value $F(t)$ is <0.85 and hence equation 5 is used to calculate Boyd number.

As per Boyd model, if B(t) vs t graph which is also called Boyd plot is non-linear, then film diffusion is the dominant mechanism, and if Boyd plot is linear passing through origin, then intra particle diffusion will be the rate limiting process. However, if Boyd plots are linear and not passing through origin, then the pore diffusion may play a dominant role [14,15].

B(t) vs t graphs are plotted for pristine and functionalized SWNTs and shown in figure 4. The linear nature of the graphs indicate that the diffusion may be mainly dominated by intraparticle diffusion.

Inter particle diffusion model

As per studies reported in literature [16,12], if a plot of ln(1-F(t)) vs t is a straight line and the intercept is equal to $ln\frac{\pi^2}{6}$, then interparticle diffusion will be the dominant process.

The graphs, ln(1-F(t)) vs t have been plotted for pristine and functionalized SWNTs. All the graphs (figure 5) are observed to be linear. However, the calculated values of C, the y-intercept (table 2) differ from the value $ln\frac{\pi^2}{6}$ =0.498. This indicates that interparticle diffusion may not be the main controlling mechanism.

Intra particle diffusion model

Weber and Moris proposed intraparticle diffusion model [17]. The equation in terms of change in conductivity can be written as

$$\Delta\sigma_t = K_{ipd}\sqrt{t} + C \quad \text{---------- (6)}$$

K_{ipd} is the rate kinetic constant for intraparticle diffusion. If weber and Moris plots show multi linearity, then more than one rate limiting mechanisms may be involved in diffusion [18]

The plots of $\Delta\sigma_t$ vs $\sqrt{t}$ are shown in figure 6 for pristine and functionalized SWNT. The plots do not show multi-linearity. The linear nature of the graph indicates that intraparticle diffusion is the main rate controlling process in adsorption of NH_3 on SWNT in both pristine and functionalized form. K_{ipd} is estimated from slopes of graphs and listed in the table 3. The rate constant increases with increase in gas concentration, however its optimum value is obtained at 0.1mg SnO_2 functionalized SWNT. This points towards the good adsorption capacity for 0.1mg functionalized SWNT.

The decrease in adsorption for 0.2mg and 1mg functionalized SWNT may be attributed to the enhanced n-type nature of SnO_2 dominating over p-type nature of SWNT by encapsulation [11]. The optimum adsorption capacity for

0.1mg SnO_2 functionalized SWNT for NO_2 gas is also observed in our earlier work [11].

FIGURES

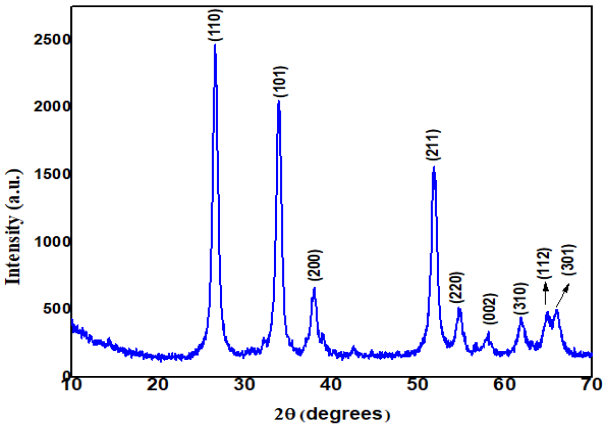


Figure 1: X ray diffraction pattern obtained for SnO_2 Nanoparticles

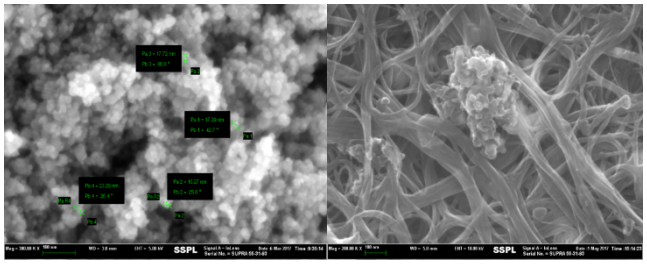
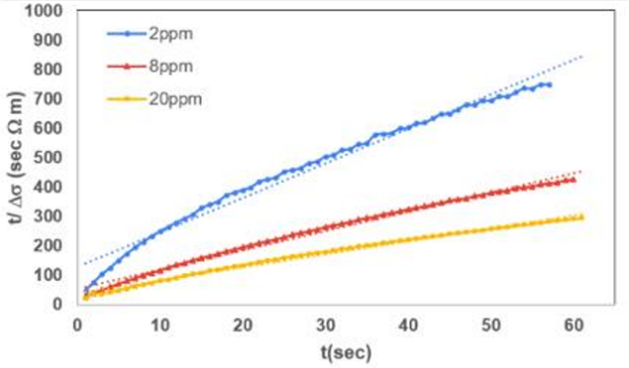
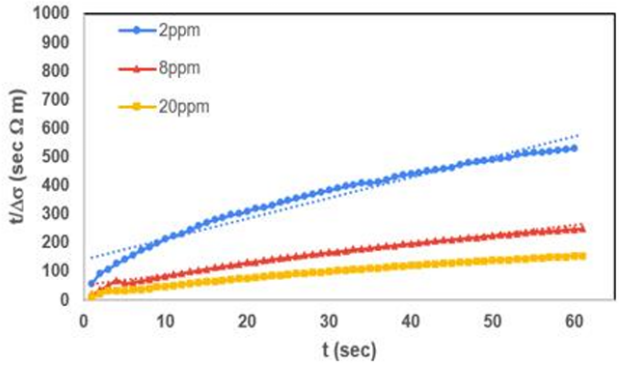


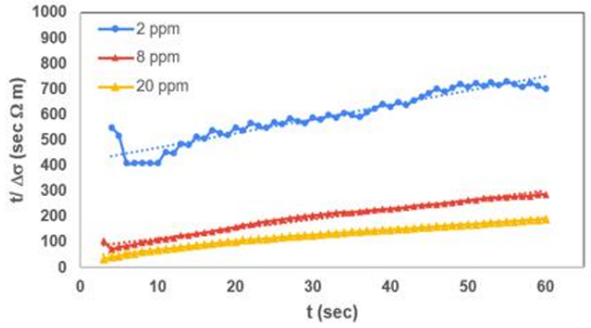
Figure 2: FE-SEM images obtained for (a) SnO_2 Nanoparticles and (b) SnO_2 functionalized CNT



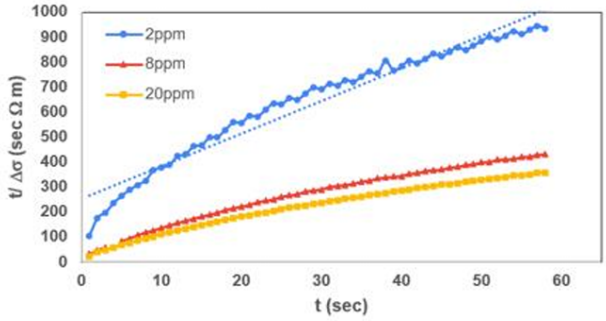
3(a)



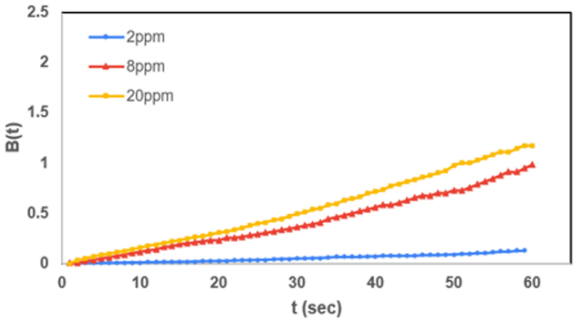
3(b)



3(c)

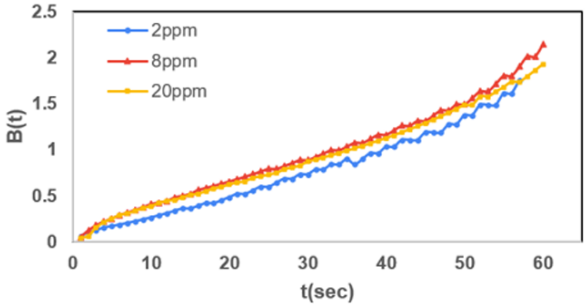


3(d)

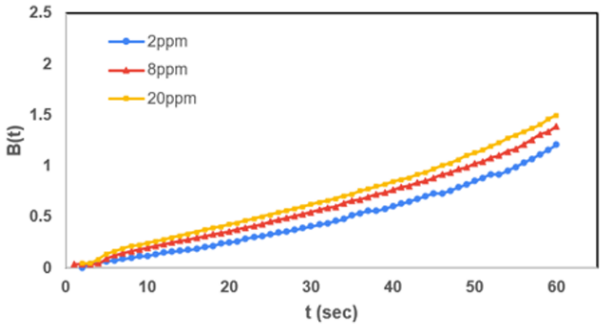


4(c)

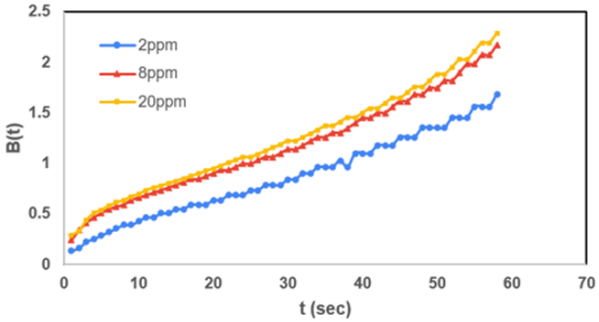
Figure 3: $\frac{t}{\Delta\sigma_t}$ vs t graphs for (a) pristine; (b) 0.1mg, (c) 0.2mg, (d) 1mg SnO_2 functionalized SWNT



4(a)

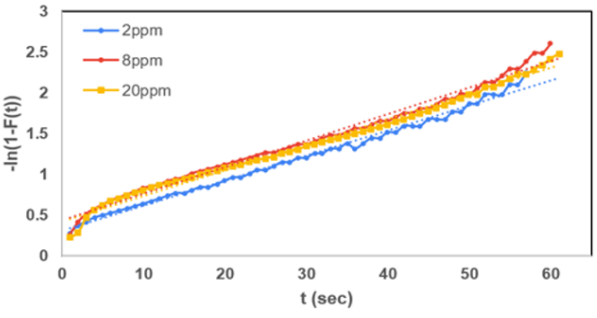


4(b)

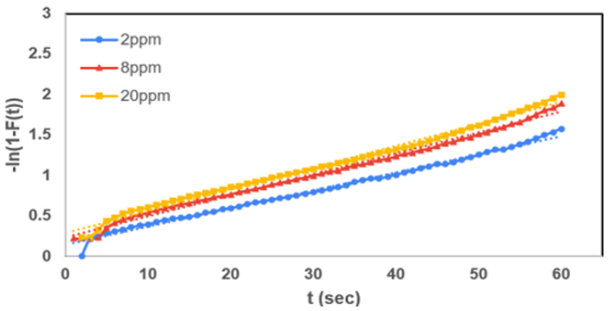


4(d)

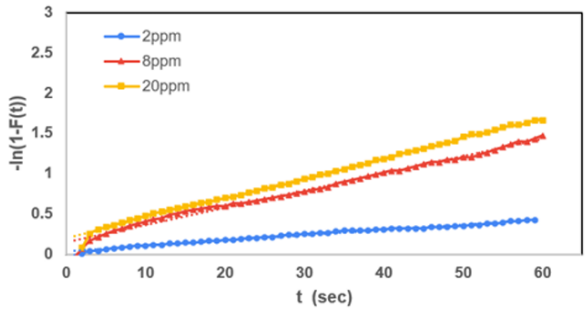
Figure 4: B(t),Boyd number vs t graphs for (a) pristine; (b) 0.1mg, (c) 0.2mg, (d) 1mg SnO_2 functionalized SWNT



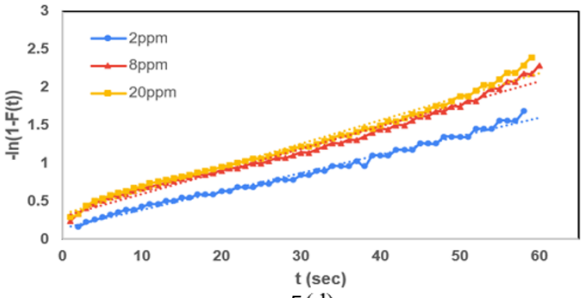
5(a)



5(b)

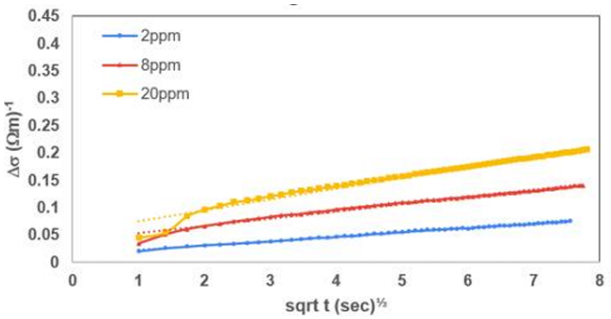


5(c)

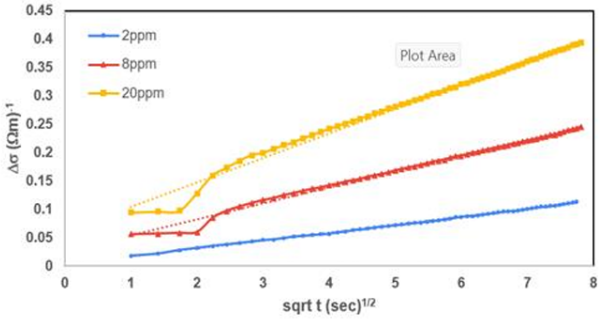


5(d)

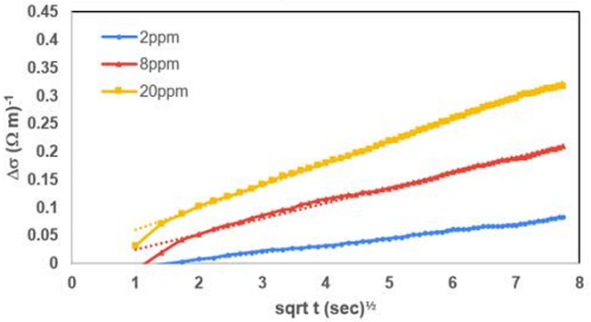
Figure 5: Plot of -ln(1-F(t)) vs t, Interparticle diffusion model for (a) pristine; (b) 0.1mg, (c) 0.2mg, (d) 1mg SnO_2 functionalized SWNT



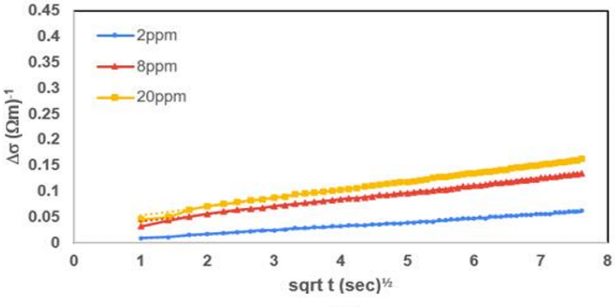
6(a)



6(b)



6(c)



6(d)

Figure 6: Plot of $\Delta\sigma$ vs $\sqrt{t}$, Weber and Morris model for (a) pristine; (b) 0.1mg, (c) 0.2mg, (d) 1mg SnO_2 functionalized SWNT

Conclusion

The dominant mechanism for adsorption of NH_3 gas on pristine and SnO_2 functionalized SWNT is seen to be governed mainly by intraparticle diffusion. The rate constant calculated for Weber and Morris model show an optimum value for 0.1 mg functionalized SWNT. The results indicate that functionalization only with a limited amount of SnO_2 is helpful in enhancing the adsorptive capacity of SWNT.

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