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Adsorption of Methylene Blue on Nano Composite MWCNTs/ZrO_2: Equilibrium, Dynamic and Surface Data

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A directly ball milling method for quick synthesis of multiwall carbon nanotubes (MWCNTs)/ZrO_2 composite was developed in this study. The adsorption ability of the composite was determined taking methylene blue as model contaminant. Results show the adsorption ability of material could be improved by almost 1.5 times by this simple method. The composite was characterized by TEM, EDS, XRD, Zeta-potential and surface area. The equilibrium adsorption isotherms, kinetic and thermodynamic properties, adsorption mechanism of the related adsorption process were investigated. Results show the adsorption reaction is a spontaneous, endothermic and physisorption process. Based on the low cost and simple peparing method, the nano composite is considered to be a promising adsorbent to treat water pollution in large scale.

Keywords: Adsorption, Carbon nanotubes, Nano composite, Methylene blue, ZrO_2.

INTRODUCTION

Dyes have been widely used in many industries, such as textile, paper, cottons, food, leather, plastics and cosmetic products. The discharge of dyes and/or their breakdown products may cause serious environmental problems. There are numerous methods have been proposed and applied in removing dye compounds from wastewater, including sono-chemical degradation[1], electro-catalytic degradation[2], chemical oxidation, flocculation, photocatalytic[3], membrane filtration[4], adsorption[5]. Among these techniques, adsorption provides simple and low-cost methods for treating the wastewater contaminated by dyes[6].

Recently, a large number of oxide powders and natural minerals have been utilized to develop low-cost and effective adsorbents to remove dyes from water. The reported results show that some of them possess high efficiency in removing dyes, providing eco-friendly, renewable and low cost ways to treat dyes pollution[7-12].

Zirconia (ZrO_2) is a typical low cost metal oxidation. It is chemically inert with excellent resistance towards acids, alkalis, oxidant and reductant[13]. Furthermore, ZrO_2 is known to be eco-friendly and biological inert and it has been used as implant[14] and dentistry[15] materials for many years. Hence, it is considered that taking this biological inert material as adsorbent in aquatic systems is less likely to cause secondary pollutions.

Carbon nanotubes (CNTs) are graphene sheets which are seamlessly rolled into cylindrical tubes[16]. They are widely applied in many areas, including used as efficient adsorbents towards various organic compounds and inorganic ions[17], But their relatively high cost limits their practical use to treat waste-water in large scale.

Several studies reported synergistic effects of carbon nanotube enhanced properties of composite, especially in ceramic researches[18-22]. However, to the best of our knowledge, there are few reports about carbon nanotubes/ZrO_2 composites used to treat water pollutions. Ntim and Mitra[16] reported a nanohybrid of multiwall carbon nanotube-zirconia with high adsorption ability to remove As(III) and As(V) from water. But content of multiwall carbon nanotube in the composite is as high as 95.15 wt. %, which costs too much and would limit its actual application.

In the present study, a novel nano composite was conveniently prepared by incorporating 0.1 wt. % multiwall carbon nanotubes (MWCNTs) with nano ZrO_2. The two components can be directly ball milled without solvent for 3 h at room temperature to get MWCNTs/ZrO_2. To investigate the adsorption ability of the nano hybrid, methylene blue (MB) was taken as model contaminant. Methylene blue is one of the most widely used dye, especially in textile industry. Being highly soluble and biologically recalcitrant, it is difficult to remove by common chemical and biological treatments. In this study,

we report the preparation, characterization and methylene blue adsorption ability of MWCNTs/ZrO_2 as well as the related kinetics, thermodynamics and mechanism study.

EXPERIMENTAL

Multi-wall carbon nanotubes (MWCNTs) were obtained from Chendou organic chemicals Co. Ltd., Chinese academy of sciences. MWCNTs' outside diameter (OD) is 10-20 nm; hydroxyl content is 3.06 wt. %; length is 10-30 μm. Nano ZrO_2 was obtained from Ganzhou qiandong rare earth group Co. Ltd.

Preparation of MWCNTs/ZrO_2: 0.1 wt. % MWCNTs were mixed with nano ZrO_2. The mixed powder was added into a 1 L milling jar containing several agate balls with diameter of 0.5 cm and was ball milled without solvent for 3 h at room temperature on a planetary ball mill (QW-3SP4 planetary ball mill, Nanjing university instrument factory). The obtained powder was prepared to 1 wt. % uniform suspension with deionized water. Then, the suspension was carefully sprayed by spray dryer (Shanghai Yacheng Instrument Co., Ltd.) with water evaporation rate of 1500 mL/h to get MWCNTs/ZrO_2 composite.

Preparation of methylene blue (MB) solution: Methylene blue trihydrate was purchased from shanghai xinshengshi chemical science Co. Ltd. and used without further purification. A series of stock solution of methylene blue (20, 30, 40, 50, 70, 100, 130 and 180 mg/L) were prepared. The concentrations of methylene blue in working solutions were measured by the absorbance at 665 nm[23] using a Unico UV-2000 UV-visible spectrophotometer. Standard calibration curves, fitted by the Beer-Lambert's law, were prepared from methylene blue solutions with different concentrations that yielded absorbance ranging from 0.1 to 1.

Effect of initial pH: The composite adsorbent was added into an Erlenmeyer flask containing methylene blue solutions. In order to investigate the effects of pH, the initial concentration of methylene blue solution was fixed at 50 mg/L and the pH values were ranging from pH 3 to 11. The initial pH values were previously adjusted with 0.12 M HCl or 0.10 M NaOH. Temperature was 298 K controlled by a thermostat rotary shaker with a constant speed of 200 rpm.

Effect of adsorbent dose: To investigate the effects of the amount of adsorbent, the initial methylene blue concentration and volume were fixed at 20 mg/L and 30 mL and the adsorbent amounts were 10, 20, 30, 35, 40, 45, 50, 60 and 70 mg, respectively.

The adsorbed amount of methylene blue per unit mass of adsorbent [Q_e (mg/g)] was calculated from the concentration difference of the solution at the beginning and at equilibrium according to the eqn. 1:

$$Q_e = (C_0 - C_e)\frac{V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of methylene blue (mg/L), respectively. V is the volume of the solution (mL) and m is the amount of adsorbent (g). The per cent of methylene blue removal was calculated using eqn. 2:

$$\text{Methylene blue removal rate (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100\ \% \quad (2)$$

Adsorption kinetics studies: The rate of dye adsorption was studied within a period as long as 180 min with solution being sampled at different time intervals. The initial concentration of methylene blue was 50 mg/L. The other experimental conditions were the same as described earlier. The removal rate of methylene blue was determined by eqn. 2. The adsorbed amount of methylene blue at intervals of time [Q_t (mg/g)] was calculated using eqn. 3, C_t was the concentration of methylene blue at intervals of time (t).

$$Q_t = (C_0 - C_t)\frac{V}{m} \quad (3)$$

Adsorption experiments: 30 mg of composite adsorbent was added into an erlenmeyer flask containing 30 mL of different methylene blue solutions at 298 K. The initial concentration of the methylene blue solution was 20, 30, 40, 50, 70, 100, 130 and 180 mg/L, respectively. pH was 7.2. Other conditions were as described before.

Nano ZrO_2 without MWCNTs was employed to the same procedure to determine its adsorption ability towards methylene blue for comparison.

Adsorption thermodynamic studies: A similar procedure as described above was employed to perform the adsorption thermodynamic studies, except the temperatures were changed to 298, 303 and 308 K, respectively.

Detection method: The composite characterized by scan electron microscopy (SEM), powder X-ray diffraction (XRD) and the surface area. X-ray energy dispersive spectroscopy (EDS) was conducted on (FEI-Quanta 200) electron microscope, XRD analysis was performed using a D8 focus XRD and the BET surface area was determined from adsorption isotherms using a surface area analyzer automated gas sorption system (V-Sorb 4800, Gold APP Instrument Corporation, China). Zeta-potential analysis was conducted on a Malvern Zetasizer NanoZS 90 instrument. Transmission Electron Microscope (TEM) detected by JEM-1011 Transmission Electron Microscope, at 100 kV by negative staining.

RESULTS AND DISCUSSION

Characterizations of the composite adsorbent: After 0.1 wt. % multi-wall carbon nanotubes being impregnated, the sample is significantly darker in colour. TEM images of the composite are shown in Fig. 1. It is observed that morphology of the adsorbent is spherical particles with about 40 nm in diameter. The results of EDS analysis (Table-1) confirm the components of the composite.

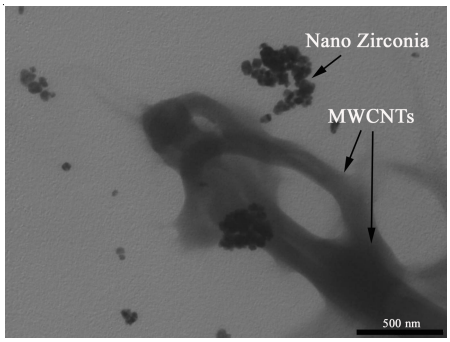

Fig. 1. Typical TEM image of MWCNTs/ZrO_2

TABLE-1
EDS ANALYSES OF ZrO_2 (WITHOUT MWCNTs) AND MWCNTS/ZrO_2

ZrO_2 (without MWCNTs)		
Element	Weight (%)	Atomic (%)
O K	35.17	75.57
Zr L	64.83	24.43
Total	100.00	100.00
MWCNTs/ZrO_2		
C K	4.32	10.78
O K	37.35	70.03
Zr L	58.33	19.18
Total	100.00	100.00

Fig. 2 shows the BET test results of zirconia and the composite. The BET surface area of the adsorbent is 25.05 (m^2/g) and the BET surface area of zirconia is 16.43 (m^2/g). It can be seen that the impregnation of MWCNTs can enhance the BET surface, which is similar to the observation in other study[24].

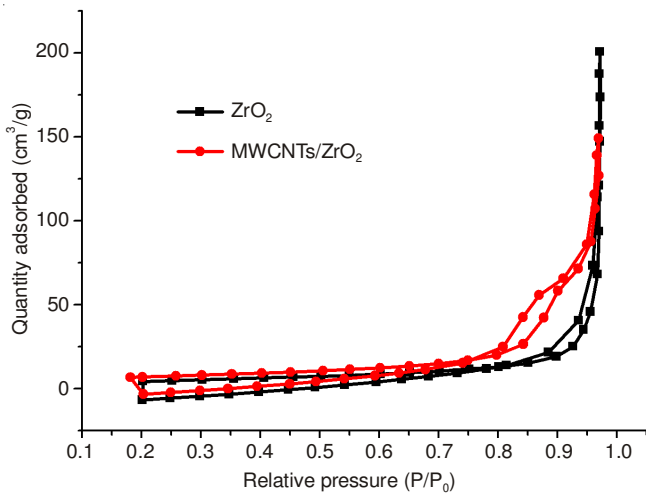

Fig. 2. Nitrogen adsorption-desorption isotherms of ZrO_2 and MWCNTs/ZrO_2

Fig. 3 shows the XRD patterns of the adsorbent. The obvious diffraction peaks located at about 28.4, 30.2, 35.0, 50.0 and 60 degree indicate the monoclinic and tetragonal phase of ZrO_2 coexist in the adsorbent.

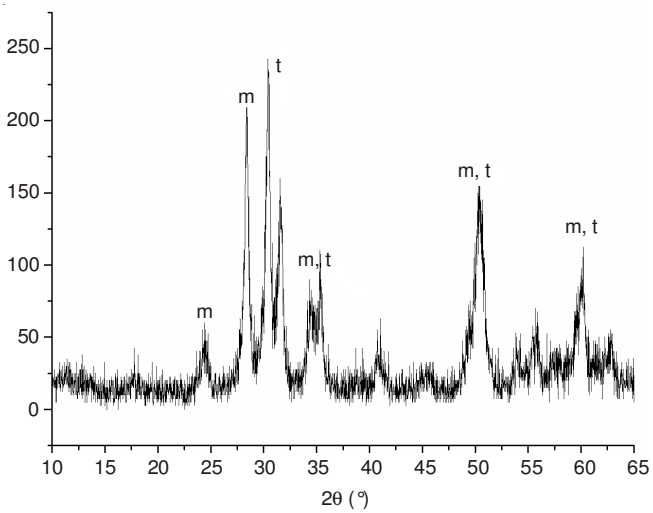

Fig. 3. XRD patterns of MWCNTs/ZrO_2

Effect of initial pH on the adsorption of methylene blue: The effect of pH on adsorption capacity of the composite is shown in Fig. 5. It can be seen that at lower pH, the increase of pH value results in the increase of the adsorption capacity. But at pH > 9, a decrease in adsorption of methylene blue is observed. Methylene blue is a cationic dye. It competed with H^+ ions to form electrostatic interaction onto the functional groups of the adsorbents at low pH conditions[25]. Consequently, in these conditions when the pH value increases, the amount of H^+ decreases and methylene blue have more opportunity to be adsorbed. Analysis of zeta-potential also gives the same results. Fig. 4 shows pH value increasing results in decrease of surface charge density. The less positive the adsorbent is, the more opportunities that cationic dye can be adsorbed. However, it is different at pH > 9, where a decrease in adsorption of methylene blue ions is observed. That is because at pH > 9, methylene blue can react with OH^- to form highly soluble hydroxyl complexes which is difficult to be adsorbed[26-28].

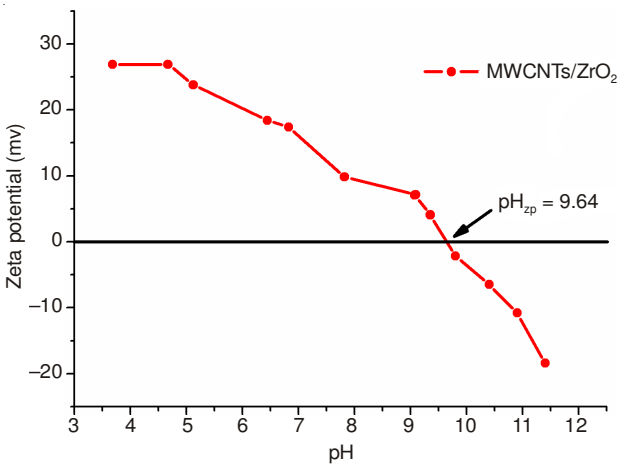

Fig. 4. pH-Zeta potential of MWCNTs/ZrO_2

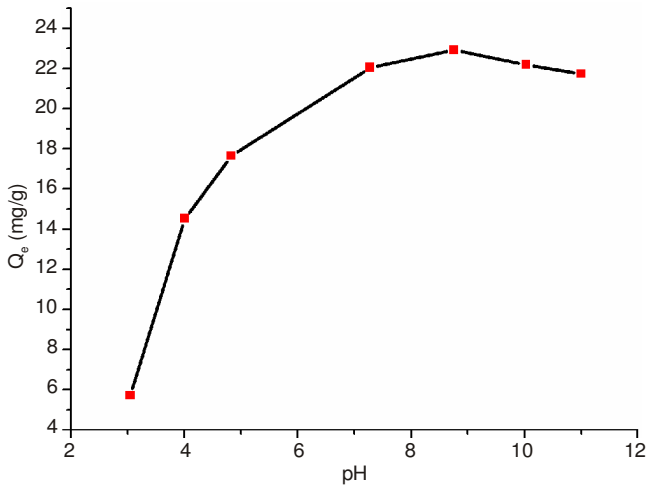

Fig. 5. Effect of initial pH on the adsorption of methylene blue by composite (Initial methylene blue concentration and volume: 50 mg/L, 30 mL, the composite weight: 30 mg)

Effect of adsorbent dose on the adsorption of methylene blue: This experiment was performed by adding different amounts of adsorbent into a certain volume (30 mL) of

methylene blue solution. Results show that adsorbent dose more than 20 mg can't significantly improve removal rate. To ensure enough adsorption, 30 mg was chosen as the amount of adsorbent.

Kinetic study: Fig. 6 shows the effect of contacting time on the dye adsorption. It is apparent from Fig. 6 that the adsorption is a quick process. The equilibrium can be reached within 0.5 h. The process appears to consist of two phases, an initial phase that the adsorption rate is very fast and a second phase that the uptake process is slower and reaches equilibrium at the end. Based on these results, 40 min is chosen as the contacting time in the following experiment.

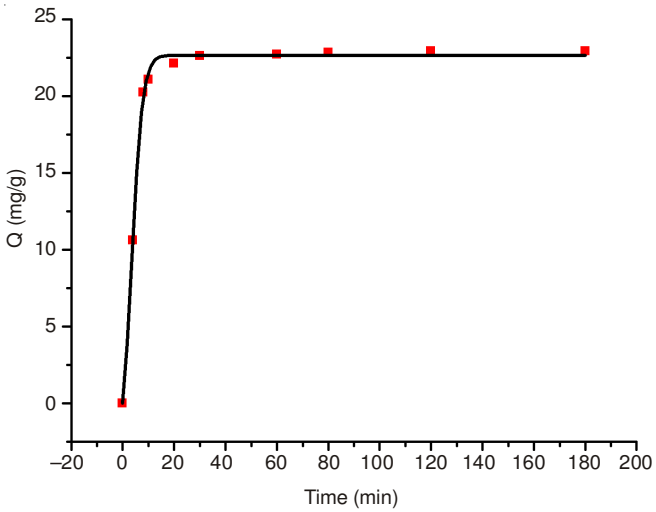

Fig. 6. Effect of contact time on adsorption of methylene blue over MWCNTs/ZrO_2

In order to investigate the controlling mechanisms of the adsorption, Largergen pseudo-first-order kinetic rate model, pseudo-second-order mechanism rate model and Weber and Morris intra-particle diffusion model were used to study the experimental kinetic data. The equation of Largergen pseudo-first-order kinetic rate model is shown below eqn. 4[29]:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

where Q_e (mg/g) and Q_t (mg/g) are the amounts of anions adsorbed at equilibrium and at different time intervals, respectively; K_1 (1/min) is the rate constant of pseudo-first-order adsorption. The linear plot of "$\ln(Q_e-Q_t)$ *vs t*" was used to estimate K_1 and Q_e from the slope and intercept.

Pseudo-second-order kinetic model is represented as[30]:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

where Q_e and Q_t are the same as described above and K_2 (g/mg min) is the rate constant of pseudo-second-order adsorption. The values of K_2 and Q_e can be determined from the slope and intercept of the "t/Q_t *vs t*" plot.

The experimental (exp) and calculated (cal) parameters of the above kinetics models are summarized in Table-2. From the data in Table-2, one can see that pseudo-second-order is more appropriate than pseudo-first-order to describe the adsorption process, because it gets correlation coefficient (R^2) closer to 1, $Q_e(Q_{e(cal)})$ closer to $Q_e[Q_e(exp)]$.

Weber and morris intra-particle diffusion model can be expressed as[31]:

$$Q_t = K_i t^{\frac{1}{2}} + C \quad (6)$$

where Q_t is the same as described above. K_i (mg/g $min^{0.5}$) is the intraparticle diffusion constant, which can be obtained from the slope of "Q_t *vs.* $t^{0.5}$" plot (Fig. 7). If the straight line passed through the origin, intra-particle diffusion would be the rate controlling step. Fig. 7 shows the line has nonzero intercept. Therefore, it is deduced that intra-particle diffusion is not the only rate-controlling step for the adsorption process. This reveals the coexistence of external film and intra-particle diffusions during the adsorption process[32].

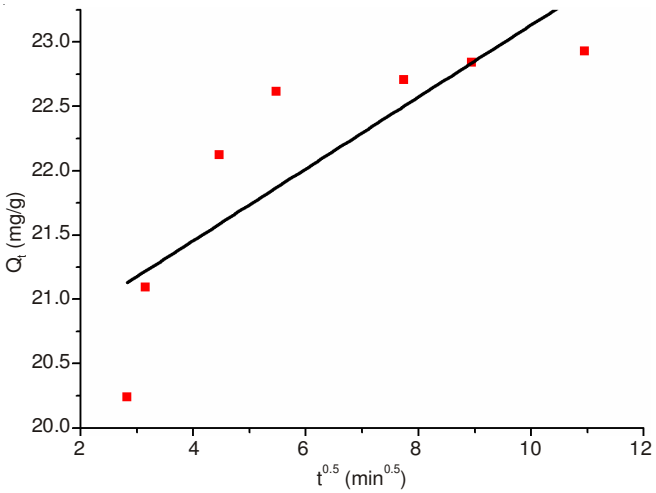

Fig. 7. Kinetic data fitted by intra-particle diffusion model

Adsorption isotherm studies: The adsorption equilibrium isotherm is important for describing how the adsorbate molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state. The adsorption isotherms of methylene blue on the adsorbent composite at 298, 303 and 308 K are shown in Fig. 8. Equilibrium uptake increases with increasing methylene blue concentration over the range of temperatures. This is a result of the increase in the driving force from the concentration gradient. The larger concentration of methylene blue in the solution, the more methylene blue ions surround the active sites, resulting in greater adsorption.

TABLE-2
KINETICS DATA OF ADSORBED OF METHYLENE BLUE TO THE ADSORBENT

Initial MB concentration mg/L)	$Q_{e\ (exp)}$ (mg/g)	Pseudo-first order			Pseudo-second order			Intraparticle diffusion	
		$Q_{e\ (cal)}$ (mg/g)	K_1 1/min	R^2	$Q_{e\ (cal)}$ (mg/g)	K_2 (g/mg min)	R^2	K_i (mg/g $min^{0.5}$)	R^2
50	22.9	4.79	-0.0535	0.798	23.2	0.0254	0.999	0.279	0.638

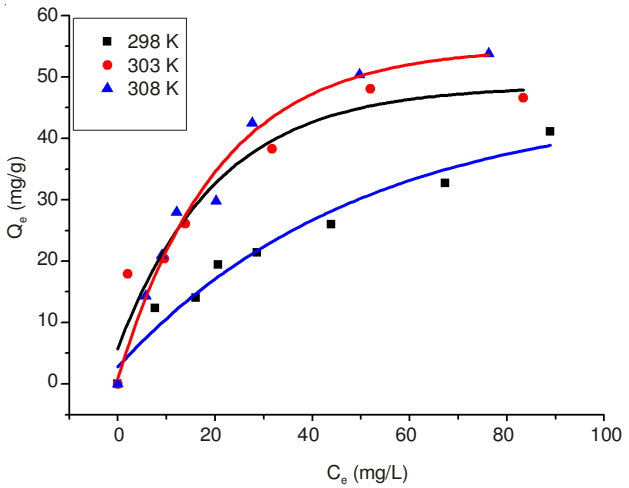

Fig. 8. Isotherm plots for the adsorption of methylene blue onto MWCNTs/ZrO_2 at different temperatures

Langmuir[33] and Freundlich[34] isotherm models were used to test the isothermal data. Langmuir isotherm assumes that the single adsorbate binds to a single site on the adsorbent and all surface sites on the adsorbents have the same affinity for the adsorbate. The adsorption process is a monolayer coverage model if the data fit well to Langmuir model. Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (7)$$

where C_e (mg/L) is the equilibrium concentration; Q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbate; Q_0 (mg/g) is the maximum adsorption ability predicted by Langmuir model and K_L (L/mg) is the Langmuir constant related to adsorption capacity and rate of adsorption. Another important parameter, R_L, called the separation factor or equilibrium parameter, is also evaluated in this study and is determined from the relation[35]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

where K_L is the Langmuir constant (L/mg) and C_0 (mg/L) is the initial dye concentration. The value of R_L indicates whether the type of the isotherm is either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values for methylene blue adsorption onto the composite are calculated to be less than 1 and greater than zero, indicating favorable adsorption (Table-3).

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. The adsorption process is multiplayer coverage if the data fit well to Freundlich model. The linear form of the Freundlich equation is:

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (9)$$

where K_F and n are Freundlich constants, n giving an indication of how favorable the adsorption process is and K_F [mg/g(L/mg)$^{1/n}$] is the adsorption capacity of the adsorbent. The slope 1/n ranging between 0 and 1 is a measure of the adsorbed intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to 0[36]. The linear plot of ln(Q_e) *versus* ln(C_e) gives the slope of 1/n and the intercept of lnK_F.

The results obtained by fitting equilibrium adsorption data using the above two models are listed in Table-3. Either Langmuir model or Freundlich model have high R^2 values more than 0.9, which indicates the experimental data can be well explained by both Langmuir model and Freundlich model. However, it has a little difference at different temperature. As the temperature increases, the data fit better to Langmuir model than to Freundlich model. It means the adsorption process is tend to multiplayer coverage at lower temperature while tend to monolayer coverage at higher temperature. Due to the high R^2 values, the maximum adsorption capacity of adsorbent could be predicted by Langmuir isotherm model.

Nano ZrO_2 without doping MWCNTs was employed to adsorb methylene blue at 298 K too. The equilibrium isotherm data were also fitted to Lanmuir isotherm. The fitting shows a high correlation coefficient (R^2) of 0.9426, indicating its maximum adsorption ability (Q_e) can be predicted by Langmuir model. The Q_e of ZrO_2 is 37.6 mg/g, which is significantly lower than that of MWCNTs/ZrO_2 (55.5 mg/g). The results clearly indicate the adsorption ability can be improved almost

TABLE-3
ISOTHERM PARAMETERS FOR THE REMOVAL OF METHYLENE BLUE BY THE COMPOSITE AT DIFFERENT TEMPERATURES

Isotherm	Parameter	C_0 (mg/L)	Temperature (K)		
			298	303	308
Langmuir	Q_0 (mg/g)	-	55.5	57.1	69.5
	K_L(L/mg)	-	0.024	0.064	0.048
	R_L	30	0.578	0.342	0.412
		40	0.507	0.281	0.345
		70	0.370	0.182	0.231
		100	0.291	0.135	0.174
		130	0.240	0.107	0.139
Freundlich	R^2	-	0.904	0.983	0.981
	K_F [(mg/g) (L/mg)$^{1/n}$]	-	4.085	8.807	6.844
	1/n	-	0.499	0.404	0.505
	R^2	-	0.958	0.914	0.928
Dubinin-Radushkevich (D-R)	X_m(mol/g)	-	6.116×10^{-4}	3.514×10^{-4}	1.050×10^{-3}
	K(mol^2/kJ^2)	-	4.240×10^{-3}	2.298×10^{-3}	3.963×10^{-3}
	E(kJ/mol)	-	10.86	14.75	11.23
	R^2		0.945	0.851	0.943

1.5 times by this composing method, which may be due to the synergistic effects of MWCNTs and ZrO_2.

In order to determine whether the adsorption is physical or chemical in nature, the equilibrium isotherm data of MWCNTs/ZrO_2 were also fitted to the Dubinin-Radushkevich (D-R) equation (eqn. 10)[37]:

$$\ln X = \ln X_m - K\varepsilon^2 \quad (10)$$

where X and X_m are the amount of methylene blue adsorbed on the adsorbent (mol/g) and maximum amount of methylene blue on the adsorbent (mol/g), respectively, K a constant related to the sorption energy (mol^2/kJ^2), ε the Polanyi potential = RT ln(1 + 1/C) [C is the equilibrium concentration of strontium ions in solution (mol/L)], R the gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T the temperature (303 K). From the slopes and intercepts of the linear graphs of lnX and ε^2, the parameters K and X_m were calculated (Table-3). The mean energy of sorption (E) is the free energy change when one mole ion is transferred to the surface of the solid, which can be calculated from[37]:

$$E = -(2K)^{-\frac{1}{2}} \quad (11)$$

It is considered that sorption process with values of E in the range of 8-16 kJ/mol is governed by ion exchange. In the case of E < 8 kJ/mol, sorption is mainly affected by physical forces. In the case of E > 16 kJ/mol, sorption process is dominated by particle diffusion course[37]. D-R constants (X_m, K and E) were calculated and listed in Table-3.

The calculated E values of methylene blue adsorption are 10.9, 14.8 and 11.2 kJ/mol for composite at 298, 303 and 308 K, respectively. These values are in the range of 8-16 kJ, suggesting the sorption courses are governed by ion exchanging.

Table-4 showed the performance of MWCNTs/ZrO_2 methylene blue adsorption compared with those of some other adsorbents reported in the literatures. One can see from Table-4 that the adsorption ability of MWCNTs/ZrO_2 is not the highest one, but the medium one. Nevertheless, with the simple preparing method (just ball milling without solvent at room temperature) and low cost (just doping 0.1 % multiwall carbon nanotubes), the MWCNTs/ZrO_2 could be considered as a promising adsorbent for removal of methylene blue from wastewater in large scale.

Thermodynamic parameters of the adsorption: The thermodynamic parameters (ΔG^θ, ΔH^θ and ΔS^θ) of the adsorption of methylene blue are calculated using equations as below (eqn. 12 and 13)[38]:

$$\ln K_D = \frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT} \quad (12)$$

$$\Delta G^\theta = -RT\ln K_D \quad (13)$$

TABLE-4
COMPARISON OF MAXIMUM ADSORPTION CAPACITY (Q_0) OF DIFFERENT ADSORBENTS TOWARDS MB

Adsorbent	Maximum adsorption capacity, Q_0 (mg/g)	References
Synthetic magnesium silicate (Florisil)	147.5	23
Citric acid-treated kenaf core fibres	131.6	38
Mdified as-prepared carbon nanotubes	101.6	31
Hazelnut shell	77.0	25
$Ce_{1-x}Zr_xO_2$/attapulgite (ATP)	50.0	11
Natural illitic clay mineral	24.9	12
$CoFe_2O_4$/MWCNT composite	11.9	29
Magnetic zinc ferrite-reduced graphene oxide composite	9.8	8
MWCNTs/ZrO_2	69.5	Present study

where R is the ideal gas constant, T is the temperature (K) and K_D is distribution coefficient calculated from the experiment data using equation below (eqn. 14):

$$K_D = \frac{\text{Equilibrium concentration of MB adsorbed on composite}}{\text{Equilibrium concentration of MB in solution}} = \frac{(C_0 - C_e) \times V}{C_e \times m} \quad (14)$$

The values of $\Delta H\theta$ and $\Delta S\theta$ are calculated from the slope and intercept of the van't Hoff plots (Fig. 9). The values of ΔG^θ, ΔH^θ and ΔS^θ are listed in Table-5.

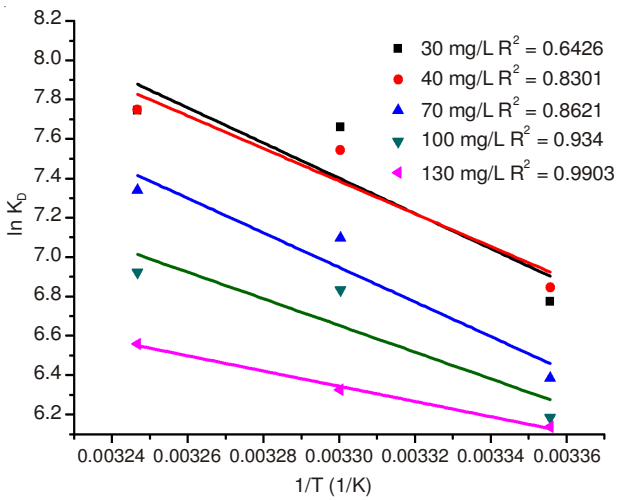

Fig. 9. van't Hoff plot of lnK *vs* 1/T for methylene blue adsorption on MWCNTs/ZrO_2

Table-5 showed the positive value of ΔH^θ suggests that the adsorption process is endothermic. The negative value of

TABLE-5
THERMODYNAMIC PARAMETERS AT VARIOUS TEMPERATURES

Concentration of MB (mg/L)	ΔHθ (kJ/mol)	ΔSθ (J/mol/K)	ΔGθ (kJ/mol)		
			298 K	303 K	308 K
30	74.40	307.04	-16.78	-19.30	-19.83
40	68.95	288.94	-16.96	-19.00	-19.84
70	73.07	298.90	-15.81	-17.87	-18.79
100	56.36	241.30	-15.33	-17.21	-17.72
130	32.17	158.90	-15.20	-15.93	-16.79

ΔG^{θ} indicates that the adsorption is spontaneous. The positive value of ΔS^{θ} confirmed the increased randomness at solid/solution interface during the adsorption process[39].

Conclusion

A novel nano composite of MWCNTs /ZrO_2 was successful prepared by direct ball milling. The results show adsorption ability of adsorbent can be significantly improved by this simple method. The adsorption reaction to methylene blue is a spontaneous, endothermic and physisorption process. This composite has great potential to be used for removal of methylene blue from wastewater in large scale. The method developed in this study is considered to be a promising way to broaden applications of both ZrO_2 and MWCNTs.

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