Synthesis of Multi-Walled Carbon Nanotubes and Its Application for Removal of Dyes

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Abstract

***Cymbopogen flexuous* oil and *Glycine max* oil, natural botanical hydrocarbons, have been found to be efficient precursors of multi-walled carbon nanotubes (MWNTs) synthesis. MWNTs were prepared by Chemical Vapor Deposition of *Cymbopogen flexuous* oil and *Glycine max* oil over well dispersed Fe/Co/Mo catalyst supported on silica. MWNTs were characterized by SEM, HRTEM, Raman spectroscopy and Nitrogen adsorption studies. Raman spectroscopy reveals that MWNTs are well graphitized. Dynamic and equilibrium studies of adsorption of Basic brown-4 on MWNTs were reported.**

INTRODUCTION

Carbon nanotubes (CNTs) have been studied extensively since they were discovered in 1991[1] and have opened a new arena science and technology in nanoscale materials. There are few reports on the synthesis of multi-walled carbon nanotubes (MWNTs) and vertically aligned carbon nanotubes from camphor, turpentine oil and pine oil [2, 3, 4]. New areas of application of nanotubes are constantly being identified ever stimulating the scientist to peep into these nanotubes. Since the discovery of multi-walled carbon nanotubes, various methods have been developed to obtain this new form of carbon [7-8]. Their synthesis methods and characterization have been studied extensively. Practical applications of carbon nanotubes require the synthesis of carbon nanotubes with certain well defined properties such as diameter distribution, alignment, filling with various materials etc. [9, 10]. To date, only purified petroleum products such as methane, benzene, acetylene, etc., are in practice for synthesizing carbon nanotubes. The advantages of using plant-derived precursors are that they can be cultivated in required quantity and there is no fear of being depleted. Kumar and Ando prepared a mixture of single-walled Carbon Nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) by thermal decomposition of botanical hydrocarbon: camphor [5]. Recently Andrews et al synthesized pure SWNTs by Chemical Vapor Deposition of camphor and its analogs [6]. *Cymbopogen flexuous oil* and *Glycine max oil* has been found to be another promising precursor for pure MWNTs synthesis. These precursors

are environmentally friendly and no chance of shortage in the near future. The method which we have been using for the synthesis of CNTs is very simple and inexpensive.

Dyes inhibit several biological processes and also color of textile effluents escalates environmental problem mainly because of its non-biodegradable characteristics. Researchers reveal that dyes can be removed completely from effluents prior to their final discharge [11, 12, and 13]. Adsorption, coagulation, electrochemical process, oxidation, precipitation, filtration, etc are the common techniques reported for the removal of dyes from effluents. Among these techniques, adsorption seems to be one of the most effective methods because of simple operation and easy handling. In this paper we report Dynamic and equilibrium studies of adsorption of Basic brown-4 on chemical vapor deposited MWNTs using natural precursors.

EXPERIMENTAL RESULTS

Synthesize of Multiwalled Carbon Nanotubes

The synthesis was carried out using a set up similar to Afre et al. [14]. Desired amounts of Fe/Co/Mo supported with silica catalyst are prepared. The catalyst on a quartz boat was placed in a quartz tube inside an electric furnace. Before switching on the furnace, nitrogen gas was purged for a few minutes for the complete removal of air from the reaction chamber .The furnace was switched on and heated to the reaction temperature 650 ^{0}C. Synthesis was conducted at 650 ^{0}C, with a typical reaction time of 30 min. The carrier gas N_2 was flushed for 10 minutes before switch on the reaction furnace to remove the inside air and create N_2 atmosphere. The reaction furnace was switched on to reach set temperature, when the furnace attained the desired temperature the N_2 gas flow was increased 100ml per min. Then *Cymbopogen flexuous oil* and *Glycine max oil* were supplied at a rate of 0.1g/min. After deposition the furnace was switched off and allowed to cool down to room temperature.

After cooling, the samples were collected. The grown carbon nanotubes were characterized by SEM, HRTEM and Raman spectroscopy. Final products obtained in each case were stored separately in vacuum desiccators until used. The resulting carbons named as CF-MWNT and GM-MWNT.

Nitrogen Adsorption Studies

The N_2 adsorption-desorption isotherms of MWNTs were measured at 77K using a gas sorption analyzer (NOVA 1000,Quanta Chrome corporation) in order to determine the surface areas and the total pore volumes[11]. The surface areas were calculated using the BET equation. Surface area of each MWNT was found to be 468 m^2/g and 452 m^2/g respectively.

Adsorption Dynamics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorb ate uptake at the solid-solution interface. The

kinetics of Basic Brown 4 adsorption on the MWNTs was analyzed using pseudo first order [15] and pseudo second order [16, 17] kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (r^2 values closer or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of Basic Brown 4 adsorption.

The pseudo First-order Equation

The pseudo first - order equation [15] is generally expressed as follows.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time t., respectively (mgg^{-1}), k_1 is the rate constant of pseudo first-order adsorption (min^{-1}).

After integration and applying boundary conditions t =0 to t = t and q_t= 0 to $q_t = q_t$, the integration form of equation (1) becomes.

$$\log(q_e - q_t) = \frac{\log(q_e) - k_1}{2.303} \times t \tag{2}$$

The value of log ($q_e - q_t$) were linearly correlated with t. The plot of log ($q_e - q_t$) Vs t should give a linear relation ship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

The Pseudo second-order Equation.

The pseudo second – order adsorption kinetic rate equation [16] is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

Where, k_2 is the rate constant of pseudo second order adsorption (g. mg^{-1}. min^{-1}). For the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (3) becomes.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_t \tag{4}$$

Which is the integrated rate law for pseudo second – order reaction. Equation (4) can be rearranged to obtain equation (5), which has a linear form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}(t) \tag{5}$$

If the initial adsorption rate h (mg g^{-1} min^{-1}) is

$$h = k_2 q_e^2 \tag{6}$$

then Equations (5) and (6) become:

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}(t) \tag{7}$$

The plot of (t/q_t) and t of equation (7) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

RESULTS AND DISCUSSION

The morphology and orientation of CNT can be easily revealed using Scanning electron microscopes. Tranmission Electron Microscpy is the powerful instrument that reveals the diameter of CNT and number of walls. Fig 1, 2 shows the SEM and TEM images of as grown nanotube from *Cymbopogen flexuous oil* and *Glycine max oil* respectively. Raman Spectroscopy is commonly employed to study the quality of the carbon nanotubes. Fig 3 represents the Raman spectra of our nanotube samples. The Sharp G-band peak and the D band peak for the Multiwalled carbon nano tubes from *Cymbopogen flexuous oil* and *Glycine max oil* respectively. G peak is assigned to E_{2g} mode of graphite lattice and D peak, due to the structural defects corresponds to an A_{1g} mode. [17, 18]. Ratios of the D peak to the G peak have been used as an indicator of the amount of disorder with nanotubes.

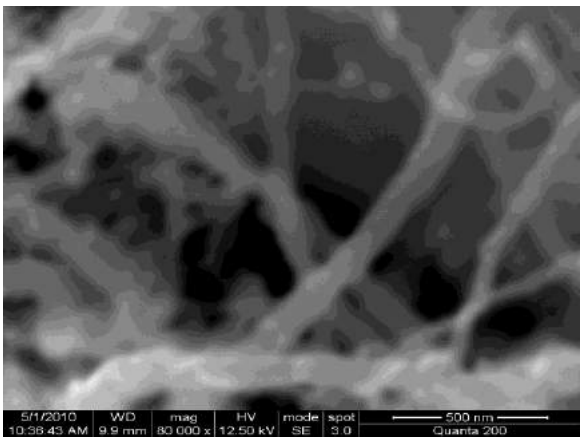


Fig. 1a. SEM image of MWNT from *Cymbopogen flexuous oil*

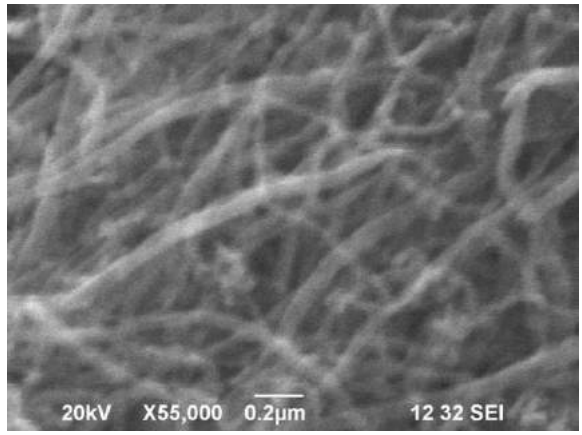


Fig. 1b. SEM image of MWNT from *Glycine max oil*

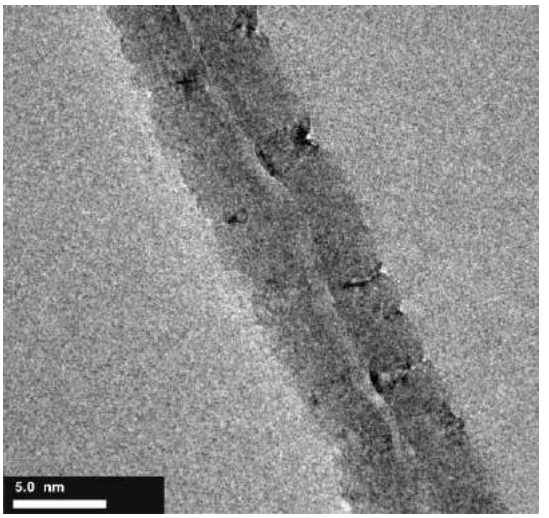


Fig. 2a. TEM image of MWNT from *Cymbopogen flexuous oil*

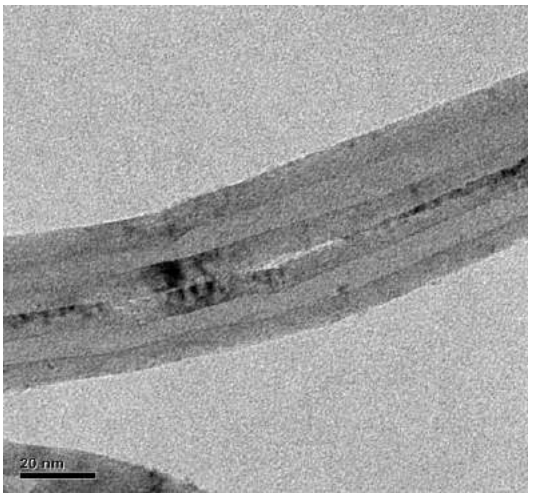
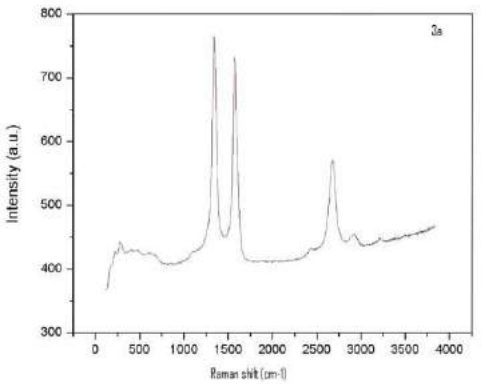


Fig. 2b. TEM image of MWNT from *Glycine max oil*



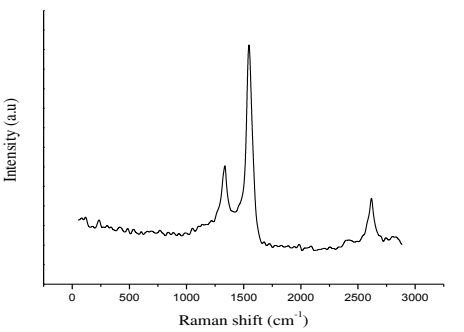


Fig 3. Raman spectra of as grown MWNTs from *Cymbopogen flexuous* and *Glycine max*

ADSORPTION STUDIES

The adsorption process for the chosen adsorbent-adsorbate system were investigated at temperature ranging from 30 to 60 ºC for each CF-MWNT and GM-MWNT. An analysis of the data reveals that the influence of temperature of the Basic Brown 4 has very little influence on the first order rate constants. The table 1 also reveals that the influence of the temperature of Basic Brown 4 on pseudo-second order rate constant is neither appreciable nor little.

Table 1. The Adsorption Kinetic Model Rate Constants for CF-MWNT and PP-MWNT

Adsorbent	**Initial Temperature**	**Pseudo first order**		**Pseudo Second order**		
		k_1 min^{-1}	**r^2**	**k_2 g mg^{-1} min^{-1}**	**h mg g^{-1} min^{-1}**	**r^2**
CF-MWNT	30^0	0.228	0.888	0.073	11.351	0.982
	45^0	0.116	0.903	6.308	5.2073	0.993
	60^0	0.192	0.891	1.568	1.662	0.984
PP-MWNT	30^0	0.181	0.903	0.129	23.614	0.989
	45^0	0.134	0.891	0.104	14.520	0.979
	60^0	0.186	0.910	0.089	12.922	0.978

It is obvious that the adsorption of Basic Brown 4 on the MWNTs is best described by pseudo second order rate equation with regression coefficient value is grater than 0.98.

ADSORPTION ISOTHERM:

The Freundlich and the Langmuir adsorption isotherms for each process were studied. The experimental value of the Longmuir constants were equated at temperature of 30, 45 and 60 ^{0}C using the well known linear form of Langmuir's adsorption isotherm equation,

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{8}$$

where, q_e is the amount of Basic Brown 4 adsorbed i.e. is equilibrium concentration of Basic Brown 4 and Q_o and b are the Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. Results show that the value of Q_o increases with increase in temperature and accounts for the endothermic nature of the on going process.

It is interesting to note that both the adsorbent exhibit similar adsorption behavior towards the Basic Brown 4.The adsorption data of Basic Brown 4 were also analyzed by the Freundlich model, given by the equation.

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \tag{9}$$

Where, q_e is the amount adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the adsorb ate (M), and K_F and n are the Freunedlich constant related to adsorption capacity and adsorption intensity respectively.

When log q_e is plotted against log C_e, a straight line with slope 1/n obtained which clearly specifies that the adsorption of Basic Brown 4 over both CF-MWNT and GM-MWNT follows the Freundlich isotherm. From these plots the Freundlich constant K_F and n are calculated and the values of theses at different temperatures are also presented in Table 2. The profile presented in the tables clearly indicates that for both the adsorption process, adsorption capacity (K_F) increases with increasing temperature.

Table 2. Freundlich and Langmuir constants of Basic Brown 4

Adsorbent	Langmuir constants						Freundlich constants					
	Q_0, mg/g			b, L/mg			n			K_F, mg g^{-1}		
	30^0C	45^0C	60^0C	30^0C	45^0C	60^0C	30^0C	45^0C	60^0C	30^0C	45^0C	60^0C
CF-MWNT	226	231	241	620	215	263	0..341	0.77	0.89	$1.3X10^{-3}$	$2.17X10^{-4}$	$2.51X10^{-4}$
GM-MWNT	210	219	220	290	292	326	0.107	0.98	0.10	$4.6X10^{-5}$	$5.26X10^{-5}$	$6.16X10^{-5}$

CONCLUSION

We have developed a simple and reproducible way of synthesizing a MWNT by CVD using botanical hydrocarbons. The high selectivity and quality of synthesized MWNTs has been confirmed by SEM and Raman analysis. The N_2 adsorption is used to determine the surface area by using BET equation. Removal of Basic Brown 4 from aqueous solution was possible using as grown MWNTs. The adsorption of Basic Brown 4 was found to be dependent on temperature, and concentration for both adsorbents. The percentage saturation was found to be almost 98 and 96% for the CF-MWNT and GM-MWNT respectively. The kinetics of Basic Brown 4 adsorption on different MWNT based adsorbents was found to follow a pseudo second-order rate equation.

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