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Synthesis of Multi-walled Carbon Nanotubes from Glycine Max Oil and Their Potential Applications

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Abstract

The discovery of carbon nanotubes has created new era in the field of nanotechnology. Spectacular properties of these nanostructured materials, stimulating scientists to peep into this tiny tube with ever increasing curiosity. The immediate challenge is to produce desired structural and characteristic featured carbon nanotubes in large quantities. Chemical vapor deposition is the most popular method of producing carbon nanotubes and it is of low-cost and highly useful technique for mass production of carbon nanotubes. These efforts requires not only chosen technique but also based on the precursor and the catalytic support. *Glycine max* oil a botanical hydrocarbon, has been found to be effective precursor for the synthesis of multi-walled carbon nanotubes (MWNTs) by Spray Pyrolysis over well dispersed Fe /Mo catalyst supported on silica at 650 °C under Ar atmosphere. As-grown MWNTs were characterized by SEM, HRTEM, Raman spectroscopy and Nitrogen adsorption studies. Raman spectroscopy revels that MWNTs are well graphitized. Dynamic and equilibrium studies of adsorption of Basic brown-4 on MWNTs were also reported.

Keywords: *Glycine max oil; Multi-walled Carbon Nanotubes; Spray Pyrolysis.*

1. INTRODUCTION

Carbon nanotubes (CNTs) have been studied extensively since they were discovered in 1991(Iijima, 1991) 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 (Karthikeyan *et al.* 2009; Mukul kumar *et al.* 2003; Rakesh *et al.* 2006). 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 (Ebbesen *et al.* 1992; Jose et al. 1993; Karthikeyan *et al.* 2010; Jose *et al.* 1993). 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 (Mukul kumar *et al.* 2003). Recently Andrews et al synthesized pure SWNTs by Chemical Vapor Deposition of camphor and its analogs(Andrews et al. 2006). *Glycine max oil* has been found to be another promising precursor for pure MWNTs synthesis. 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 (Choi *et al.* 2000). 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

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chemical vapor deposited MWNTs using natural precursors.

2. EXPERIMENTAL RESULTS

2.1 Synthesize of Multiwalled Carbon Nanotubes

The synthesis was carried out using a set up similar to Afre et al. desired amount of Fe/Mo supported with silica catalyst on a quartz boat was placed in a quartz tube inside an electric furnace(Afre *et al.* 2005). Synthesis was conducted at 650 ˚C in nitrogen atmosphere, with a typical reaction time of 30 min. *Glycine max oil was* supplied at a rate of 0.1g/min. As grown carbon nanotubes were characterized by SEM, HRTEM and Raman spectroscopy.

2.2 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 (Choi *et al.*, 2000). 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.

2.3 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 and pseudo second order kinetic models (Chien *et al.* 1980; Ho *et al.* 2000, Lagergren 1898). 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.

2.4 The pseudo First-order Equation

The pseudo first - order equation is generally expressed as follows (Lagergren 1898).

$$\log(q_e - q_t) = \frac{\log(q_e) - k_1}{2.303} \times t \tag{1}$$

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}). 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 relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

2.5 The Pseudo second-order Equation.

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

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

where, k_2 is the rate constant of pseudo second order adsorption (g. mg^{-1}. min^{-1}).

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

$$h = k_2 q_e^{\,2} \tag{3}$$

The plot of (t/q_t) and t of equation (3) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

3. RESULTS AND DISCUSSION

Scanning electron microscopy and Raman spectroscopic techniques were used to characterize the carbon nanotube produced. Fig 1, 2 shows the SEM and HRTEM images of MWNTs synthesized. Fig 3. Shows XRD of CNTs. As evident from the Fig 4. CNTs related peaks are detected at 2θ = 26.16 ˚ and 44.65 ˚ which represent graphite (002) and (101) peaks respectively. Raman spectroscopy is a powerful technique for learning the graphitic structure of the CNTs. The Raman spectra of carbon based materials mainly exhibit two main first order peaks assigned to G band and D bands. Fig 4. Shows D-band at1362.57cm $^{-1}$ and G-band at 1594.27 cm $^{-1}$. The I_D/I_G ratio as calculated from the Raman spectra of the CNTs grown in the present studies is 0.97 (Hiura *et al.* 1993; Tuinstra *et al.* 1970).

The adsorption process for the chosen adsorbent-adsorbate system was investigated at temperature ranging from 30 to 60 ºC for grown MWNTs. 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.

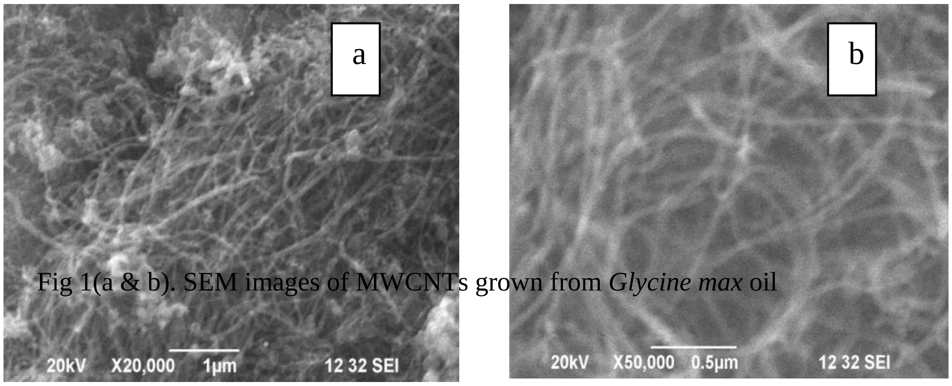

Fig 1(a & b). SEM images of MWCNTs grown from *Glycine max* oil

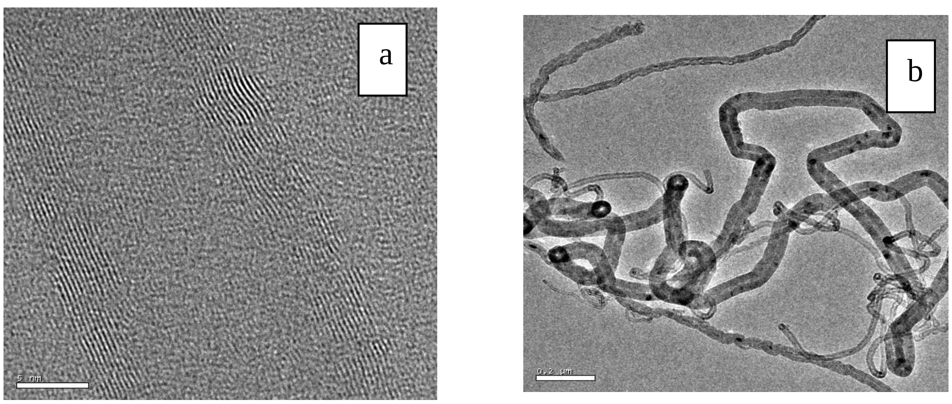

Fig 2 (a & b). HRTEM images of MWCNTs grown from *Glycine max* oil

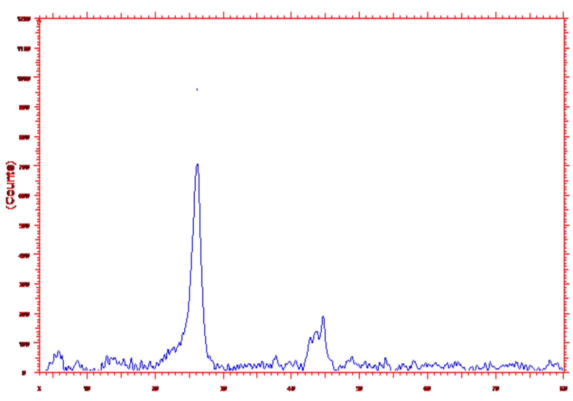

Fig 3. XRD spectra of as grown MWCNTs

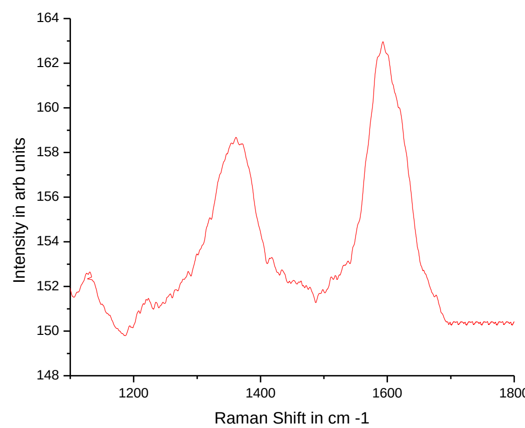

Fig 4. Raman spectra of as grown MWCNTs

ADSORPTION STUDIES

Table 1. The Adsorption Kinetic Model Rate Constants for MWNTs

Adsorbent	Initial Temperature, ˚C	Pseudo first order		Pseudo Second order		
		k_1, L min^{-1}	r^2	k_2, g mg^{-1} min^{-1}	h, mg $g^{-1}min^{-1}$	r^2
As grown MWNT	30	0.228	0.888	0.073	11.351	0.982
	45	0.116	0.903	6.308	5.2073	0.993
	60	9.192	0.891	1.568	1.662	0.984

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

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{4}$$

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 Longmuir 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.

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \tag{5}$$

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 MWNT follows the Freunedlich isotherm. From these plots the Freunedlich 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 Longmuir constants of Basic Brown 4

Adsorbent	**Temperature, ˚C**	**Longmuir constants**		**Frundlich constants**	
		$Q_°$, mg/g	**b, L/mg**	**n**	**K_f, L/g**
As- grown MWNT	30	226	620	0.341	1.3×10^{-3}
	45	231	215	0.77	2.17×10^{-4}
	60	241	263	0.89	2.51×10^{-4}

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 % for the as grown MWNTs.. 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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