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Synthesis, Characterization and Comparative Adsorbent Study of Carbon Nanotubes, Graphene and Graphite

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***Abstract*— Carbon Nanotubes are allotropes of carbon. They are tubular in shape, made of graphite. The objective of this work was to produce carbon nanotubes at room temperature without any hazardous and high energy requiring operating conditions using Staudenmier's process. There was successful synthesis of graphene as well from the same process. Characterisation of CNTs and graphene was done using Scanning Electron Microscope (SEM) analysis. Batch adsorption studies were used to study adsorption of methyl violet from a solution using carbon nanotubes. Langmuir and Freundlich adsorption isotherms were developed to analyse the equilibrium adsorption data. The study resulted that Langmuir isotherm was a better fit to the adsorption. The adsorption studies of carbon nanotubes were compared to graphene and graphite. CNTs have shown highest adsorption capacity (K_F) of 39.27 mg/g and the value of constant n is 2.07 which indicates good adsorption characteristics for Freundlich adsorption model. The adsorption capacity of carbon nanotubes for Langmuir adsorption isotherm was 169.9 mg/g and % adsorption was 78.6% which were highest among the three i.e CNTs, graphene and graphite.**

***Index Terms*— Adsorption isotherms, Carbon Nanotubes, Graphene, Graphite.**

I. Introduction

Carbon is the element in the periodic table that provides the basis for life on Earth. Elemental carbon exists in two natural allotropes, diamond and graphite. It was also discovered that carbon atoms can form long cylindrical tubes known as carbon nanotubes or CNT for short. These molecules are shaped like a tube; imagine a sheet of graphene rolled into a tube. Carbon nanotubes have a very wide range of electronic, thermal, and structural properties. These properties vary with the diameter, length, chirality or twist and wall nature of these nanotubes.

Most part of the academic literature attributes the discovery of carbon nanotubes to Sumio Iijima of Nippon Electric Company in 1991.

Carbon nanotubes are classified in two types

1. SWNTs- Single walled carbon nanotubes.
2. MWNTs- Multiple walled carbon nanotubes.

Carbon nanotubes are sheets of graphene rolled to form seamless cylinders. Carbon nanotubes are again classified based on the way the graphene sheets are wrapped into three types – armchair, chiral and zigzag.

General methods of production for Carbon nanotubes include Arc Discharge Method, Laser Ablation and Chemical Vapor Deposition.

Adsorptions of various gases, liquids or metals onto carbon nanotubes, and interactions between them, have attracted much attention recently.

II. Literature Review

A brief summary of literature review related to the theme of present work is given below.

A. Preparation of Carbon Nanotubes From Graphite Powder At Room Temperature[8]

A new chemical route to prepare carbon nanotubes at room temperature is developed. Graphite powder is immersed in a mixed solution of nitric and sulfuric acid with potassium chlorate. After heating the solution up to 70°C and leaving them in the air for 3 days obtained carbon nanotube bundles are obtained. This process could provide an easy and inexpensive method for the preparation of carbon nanotubes.

B. Carbon nanotubes: properties and application[9]

Carbon nanotubes are unique tubular structures of nanometer diameter and large length/diameter ratio. The nanotubes can be metallic or semiconducting depending on their structural parameters. This opens the ways for application of the nanotubes as central elements in electronic devices including field-effect transistors (FET), single-electron transistors and rectifying diodes. Possibilities for using of the nanotubes as high-capacity hydrogen storage media were also considered. This report is intended to summarize some of the major achievements in the field of the carbon nanotube research both experimental and theoretical in connection with the possible industrial applications of the nanotubes.

C. Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes[10]

In this work, batch adsorption experiments were carried out for the removal of methylene blue as a basic dye from aqueous solutions using carbon nanotubes (CNTs). The adsorption kinetic data were analysed using pseudo-first-order, pseudo-second-order and Elovich models. It was found that the pseudo-second order kinetic model was the most appropriate model, describing the adsorption kinetics. Adsorption isotherm of methylene blue onto the CNTs was determined at 290, 300 and 310 K with 10 mg L-1 as initial concentration of methylene blue. Adsorption equilibrium was attained within 120 min. Equilibrium data were fitted to the Langmuir, Freundlich, Temkin and Sips isotherm models and isotherm constants were determined. The equilibrium data were best represented by the Sips isotherm model. Thermodynamic parameters such as changes in the free energy of adsorption (G), enthalpy (H) and entropy (S) were calculated. The negative values of G indicate that the methylene blue adsorption process is spontaneous in nature and the positive value of H shows the endothermic nature of the process.

D. Adsorption behavior of methylene blue on carbon nanotubes[11]

The effect of temperature on the equilibrium adsorption of methylene blue dye from aqueous solution using carbon nanotubes was investigated. The equilibrium adsorption were analysed using two widely applied isotherms: Langmuir and Freundlich. The results revealed that Langmuir isotherm fit the experimental results well. Kinetic analysis were conducted using pseudo-first and second-order models and the intraparticle diffusion model. The regression results showed that the adsorption kinetics were more accurately represented by pseudo-second order model. Standard free energy changes (ΔG^o), standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) were calculated using adsorption equilibrium constants obtained from the Langmuir isotherm at different temperatures. Results suggested that the methylene blue adsorption on CNTs was a spontaneous and endothermic process.

III. Present Work

The objective of the present work is to produce carbon nanotubes using conventional chemical method i.e. Staudenmier's process followed by characterization and effectiveness studies. It is also extended to compare its adsorbent properties with adsorbents such as graphite and graphene.

A. Synthesis of Carbon Nano Tubes and Graphene

The flowsheet for synthesis of CNTs and graphene is as shown in Fig. 1:

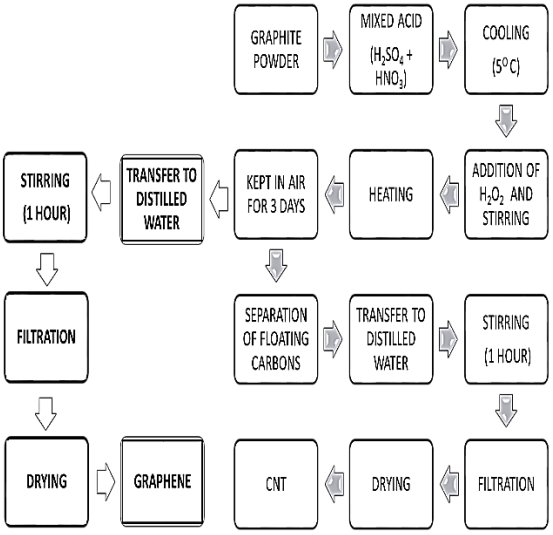

Figure 1: Flowsheet of methodology followed

B. Procedure

5 g of graphite powder was slowly added to a mixture of Nitric acid (25 ml) and Sulphuric acid (50 ml) for 30 min. The mixture was cooled in an icebath to around 5°C. After this 9.4 ml of Hydrogen peroxide was added with simultaneous stirring for 30 min. A lot of heat was produced during this step. The solution was heated upto 70°C for 24 hours and placed at room condition for 3 days. Floating carbon particles were seen in solution. These were transferred to 1 litre of distilled water. After stirring it for 1 hour the solution was filtrated and sample was dried to obtain CNTs. When complete solution was transferred to distilled water and same further process was followed graphene was obtained as product.

C. Characterization

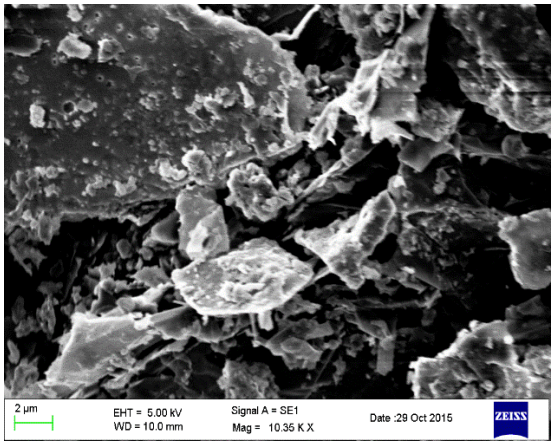

Fig 2: SEM image of CNT

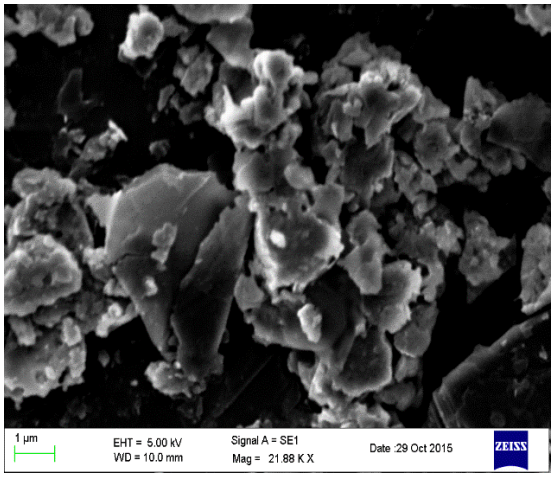

Fig 3: SEM image of CNT

The sample of Carbon nanotube was analysed using Scanning Electron Microscope (SEM). The figure nos. 3.2 & 3.3 shows SEM images. It can be interpreted that several sheets are visible with sharp edges along with tube-like structures. So there is indication of possible formation of CNTs.

D. *Adsorption Studies*

In present work the adsorption characteristics of carbon nanotubes is explored and its effectiveness is compared with some of the conventional adsorbents such as graphene and graphite powder.

1) *Materials And Methods*

a) *Adsorbent*

(1) Carbon nanotubes synthesized the lab.
(2) Graphene synthesized in the present work.
(3) Commercial grade Graphite powder.

(1)

b) *Adsorbate*

A cationic dye, Methyl Violet, having molecular formula $C_{24}H_{28}N_3Cl$ was chosen as adsorbate. Methyl Violet water solubility as 50 g L–1 (20°C) and molecular weight as 393.5 g. Methyl Violet has chosen in this study because of its known strong adsorption onto solids. The dye stock solution was prepared by dissolving accurately weighted methyl violet in distilled water to the concentration of 50 mg L^{-1}.

2) *Adsorption Equilibrium experiments*

Batch adsorption experiments were performed. Solutions of 20 mg of CNTs, graphene and graphite with 150 ml of methyl violet solutions of increasing concentrations from 5 mg/l to 40 mg/l were used. The mixtures were agitated for 20 minutes. At the end of equilibrium period, the solutions were centrifuged for the carbon nanotubes to be separated from solution later analysis of the dye concentration. The amount of methyl violet adsorption at equilibrium q_e (mg/ g) was calculated from the following equation:

$$q = \frac{(Co - Ce)V}{W}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used.

3) *Observations and Calculations*

a) *Standardization of Colorimeter*

Colorimeter was used for the analysis purpose in density of a solution containing methyl violet. Optical densities of solution samples were estimated. After the adsorption experiments were done, optical densities of solutions remained after adsorption was estimated. A graph is plotted between concentration versus optical densities and is referred as standardization graph. Using the standardization graph and referring optical densities, the final concentrations of the solutions were estimated. The standardization graph is given in Fig. 4

Table 1: Observations and Calculations

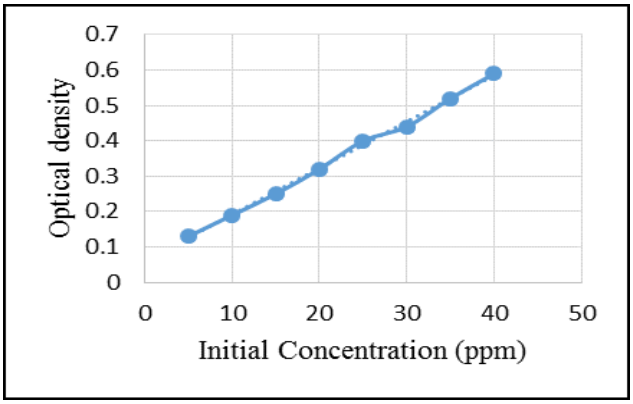

Fig. 4 Standardization graph

b) *Calculations*

Optical densities of solutions after adsorption is calculated. Standardization graph is used to estimate the concentrations of these solutions. From the initial and final value of the concentration, the % adsorption was calculated using the formula:

$$\% \text{ adsorption} = \frac{C_0 - C_e}{C_0} * 100$$

Where C_o and C_e are initial and final dye concentrations.

Further, the uptake capacity of adsorbent was calculated using the formula

$$q = \frac{(Co - Ce)V}{W}$$

The values are tabulated in Table I.

Table I: Observations and Calculations of Adsorption Isotherms

Adsorbent	Concentrati-on of original solution (ppm)	Optical density of original solution	Optical density of solution after adsorption	Concentrat-ion of solution after adsorption	% Adsorption	Uptake capacity of adsorbent (mg adsorbate/g adsorbent)
CNT	5	0.13	0.08	1.2	76	28.5
	10	0.19	0.09	2.14	78.6	58.95
	15	0.26	0.1	3.22	78.53	88.35
	20	0.32	0.12	4.3	78.5	117.75
	25	0.39	0.18	9.3	62.8	117.75
	30	0.46	0.23	12.5	58.33	131.25
	35	0.52	0.27	16.08	54.06	141.9
	40	0.59	0.34	21.44	46.4	139.2
GR	5	0.13	0.08	1.1	78	29.25
	10	0.19	0.10	3.19	68.1	51.08
	15	0.26	0.13	5.59	62.73	70.58
	20	0.32	0.17	8.41	57.95	86.93
	25	0.39	0.21	10.96	56.16	105.3
	30	0.46	0.26	15.3	49	110.25
	35	0.52	0.32	20	42.86	112.5
	40	0.59	0.40	26	35	105
GE	5	0.13	0.09	2.4	52	19.5
	10	0.19	0.13	5	50	37.5
	15	0.26	0.17	8.14	45.73	51.45
	20	0.32	0.21	11.35	43.25	64.88
	25	0.39	0.26	14.74	41.04	76.95
	30	0.46	0.32	19.6	34.67	78
	35	0.52	0.37	23.21	33.69	88.43
	40	0.59	0.44	29	27.5	82.5

4) Results and Discussions

a) Adsorption isotherms

The adsorption isotherm of Methyl Violet on CNTs is shown in Fig. 5. As can be seen, equilibrium uptake increased with increasing the equilibrium methyl violet concentrations for the experimental range. This may be a result of the increase in the driving force in the form of concentration gradient. The similar nature of isotherm is observed for other adsorbents graphite and graphene as well. However, for the same equilibrium concentrations of methyl violet in solutions, the uptake is highest for CNT followed by graphene and lastly graphite.

The adsorption studies data were fitted to the Langmuir and Freundlich isotherms as shown in Fig. 6 & 7.

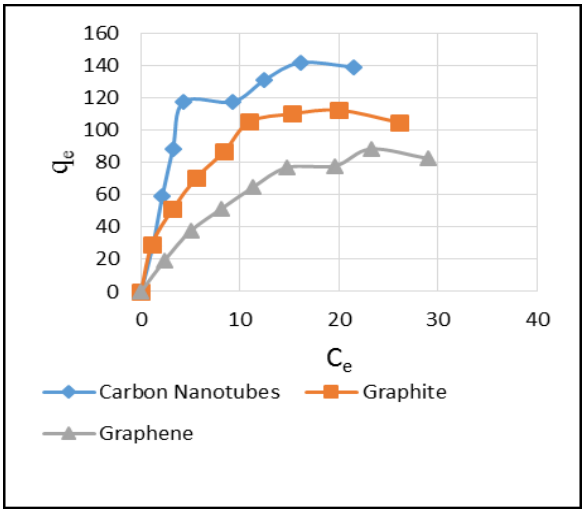

Fig. 5 Adsorption isotherms of Methyl Violet on CNTs, Graphene and Graphite

The Langmuir constants K_L and q_0 were calculated and are given in Table II. Furthermore, the effect of the isotherm shape is considered with a view to predict whether an adsorption system is favorable or unfavorable through another important parameter, R_L, called the separation factor. R_L values for methyl violet adsorption onto CNTs were less than 1 and greater than zero indicating favorable adsorption.

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface. The studied materials are good adsorbents, as n is more than 2. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to 0 (Haghseresht and Lu, 1998). The plot of ln q_e versus ln C_e is shown in Fig.7 which is a straight line indicating that the adsorption follows the Freundlich isotherm as well. Accordingly, Freundlich constants (K_F and n) were calculated and listed in Table II.

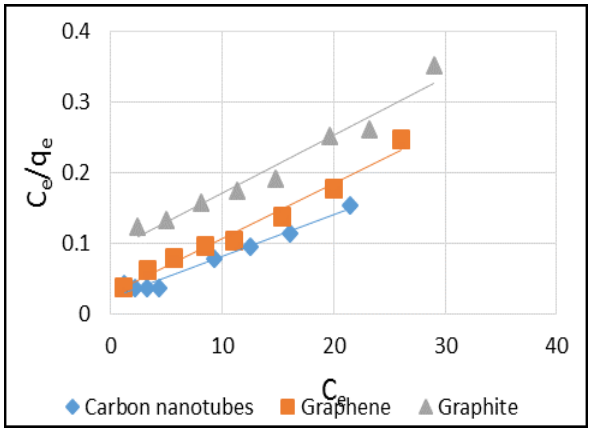

Fig. 6 Langmuir isotherm for Methyl Violet dye adsorption on CNTs, Graphene and Graphite

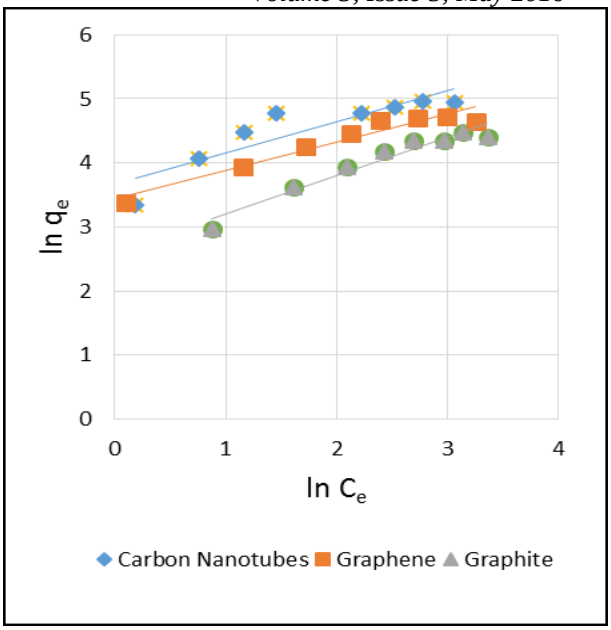

Fig. 7 Freundlich isotherm for Methyl Violet dye adsorption on CNTs, Graphene and Graphite

The results obtained in this study with those in present work are comparable with the literature reported values and is indicative of successful synthesis of CNTS and graphene. From the Table II, it is clear that for Langmuir isotherm and Freundlich isotherm, CNTs have highest adsorption capacities q_o and K_F respectively.

IV. CONCLUSION

The present work is aimed at CNT and graphene synthesis using Staudenmier's process and comparative adsorption studies. The SEM images are indicative of CNT and graphene formation.

The adsorption studies for CNTs show that Langmuir adsorption isotherm is a better fit then the Freundlich adsorption isotherm.

The comparative adsorption studies show that CNTs have high adsorption capacity of 169.48 mg/g and high % adsorption of 78.6% compared to graphene and graphite and hence are a better adsorbents.

Thus synthesis of Carbon Nanotubes from a chemical conventional method provides us with an economic and better alternative in removal of dyes from waste water.

Table II: Isotherm constants

Isotherms	Parameters	Graphite	Graphene	CNTs
Langmuir	q_o (mg/g)	121.9512	128.2051	169.4915
	K_L(mg/L)	0.3694	0.3514	0.2658
	K_L(mg/mol)	145.3468	138.2568	104.5788
	R^2	0.9642	0.981	0.9739
	R_L	0.0634	0.0664	0.086
Freundlich	K_F(mg/g(L/mg)$^{1/n}$)	13.54	31.08	39.27
	n	1.6753	2.266	2.0687
	R^2	0.9423	0.9355	0.8009

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