Asian J. Exp. Sci., Vol. 22, No. 2, 2008, 75-88

Hydrogen Adsorption by Carbon Nanomaterials from Natural Source

Maheshwar Sharon*[1], Sunil Bhardwaj[1], Sandesh Jaybhaye[1], D.Sathiyamoorthy[2], K.Dasgupta[2] and Madhuri Sharon[3]

1. Nanotechnology Research Lab., Birla College, Kalyan 421304, India
2. Powder Metallurgy Division, BARC, Trombay, India 400 085
3. Monad Nanotech, 704 A-702 Bhawani Towers, Adishankaracharya Marg, Powai, Mumbai 400 076, India.
   E-mail : *sharon@iitb.ac.in, s_p_bh@rediffmail.com*

Abstract : Carbon nanomaterials are getting importance in various applications such as hydrogen storage, fuel cell, electron field emitter etc. In order to make the cost of the gadgets utilizing carbon nanomaterials economical, efforts are being made to synthesize them at lowest possible cost. In addition, most of the processes which are being developed use precursors which are derived from petroleum products, which is destined to get depleted one day. Hence, synthesis of carbon nanomaterials based on such precursors will also get depleted and the technology based on carbon nanomaterials will come to a halt. Considering these two factors, we are making efforts to search for precursors which are plant derived and could give the desired type of products at an economical rate. Another advantage of using precursors derived from plant based materials like oil seeds, plant fibers (coconut fiber or bagasse etc) is that these materials possesses different types of morphology e.g. channel type hollow cylindrical fibers, or various types of structures having various orientation of pores etc. These varied morphologies may have some useful properties like storing of hydrogen gas, intercalating of lithium etc. Moreover, such type of structure would be extremely difficult to synthesize in laboratory.

In this paper, we report the utilization of some plant based fibers and some oil seeds to make carbon nanomaterial by pyrolysing them at very high temperature in an inert atmosphere, and characterize them by SEM for their morphology. It was observed that carbon nanomaterials obtained from fibers based precursors like coconut fiber; baggas etc have fibrous structure whereas carbon Nano materials formed from seeds of different plants show very complicated porous carbon structures. These carbon materials are being utilized for the application of Hydrogen Storage. In order to compare the utilities of plant derived carbon nanomaterials, acetylene and alcohol have also been used to prepare carbon Nano materials by the pyrolysis. However, unlike plant based precursors, these precursors needed suitable catalysts, which adds to the cost The fibrous carbon from Bagasse (*Saccharum officinarum*) gave hydrogen adsorption of 0.656 wt% at 11kg/m^2 pressure of hydrogen which is nearly the same as observed with carbon nanomaterials obtained from acetylene (0.51 wt%), suggesting that plant derived precursors can be used for such purpose. Efforts are made and presented in this paper to discuss the role of surface area and pore sizes in facilitating hydrogen adsorption.

Key words: Carbon Nanotube, Natural Precursors, Hydrogen Adsorption, Bagasse (*Saccharum officinarum*)

Introduction

Hydrogen, the most abundant element in the universe, has great potential as an energy source. Unlike petroleum, it can be easily generated from renewable energy sources. It is nonpolluting and forms water as a harmless by product during use. This makes it very attractive transportation fuel. In the Table-1 relative power density of hydrogen is given to show the importance of hydrogen as compared to other fuels.

Table 1 : Relative power density of hydrogen

Fuel	Kwhr/kg
H_2 (156 atm)	83.4
Propane	1.96
Methanol	1.45
NH_3	1.87

One still unsolved problem for the use of hydrogen, as clean fuel is the safe and efficient storage of hydrogen. One of the useful materials for transportation and storage of hydrogen has been an alloy that can absorb and hold large amounts of hydrogen by bonding with hydrogen and forming hydrides. Metal hydride though effective, but costwise not very attractive. Moreover weight of container is also not very suitable. Therefore, search has been to find another suitable material, which can adsorb at least as much as metal hydride, if not more but should be economical and light weight. Compared to metal hydride, carbon nano-materials being light weight, is sought as a better and promising material to store hydrogen.

The US Department of Energy has stated that carbon materials need to have a storage capacity of 6.5 wt% to be practical for transportation uses. Carbon nano-materials can exist as carbon nanotubes (of different diameters and various morphologies), carbon Nano-beads (of different diameter) and carbon Nano-fibers. Most of the reports available in literatures have dealt with carbon nanotubes. It is therefore, interesting to study the adsorption process with other forms of carbon nano-materials like Nano-beads, Nano-fibers.

There have also been reports that efficiency of adsorption enhances by suitable activation of carbon Nano-materials. Most of the activation has been done with either sulphuric acid or KOH. It is also possible to activate these materials with different group like OH^-, COO^-, SO_3H^- as well as different metals can be filled in CNTs. Under this project efforts would be made to establish as to which forms are most suitable for hydrogen storage and which of the activation process enhances the adsorption/desorption process.

Preparation of Carbon Nanomaterials

Authors have adopted a separate route to produce Carbon Nanomaterials from natural sources. They have been using camphor, turpentine oil for this purpose. Encouraged by this work it was thought to pyrolyse various part of the plants like seed, stem and oil of different plant to examine which part of the plant and its type gives a better Hydrogen Adsorption capacity. Because, structure of carbon Nanomaterials obtained by pyrolysis of seed or stem of plants depend upon the structure of seed and stem. Moreover, no catalyst is needed for the formation of carbon Nanomaterial. The selected plant materials are given in Table-2. As the water is the main constituent of the plant based precursors, to remove water from seeds and agricultural waste the samples are cut into small pieces and kept in a hot air oven at 100^o C for drying for six hours. This removes water and some volatile matters from these materials. Pyrolysis is done by simple Horizontal furnace. The diagram of Furnace is shown in Fig.1.

Dried product is kept in the quartz boat and inserted in the quartz tube. Then the tube is kept in the furnace and inert gas is started for 10 minutes to make inert atmosphere. If

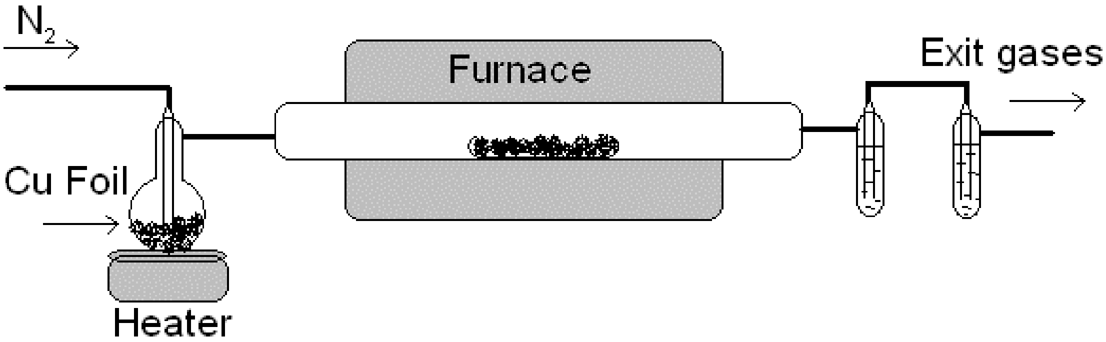


Fig. 1 : Furnace for the preparation of CNMs

the gas contains impurity of Oxygen it is passed over the heated Copper foils. The flow of the gas is maintained to 50 cc/min throughout the experiment then heating is started, temperature is maintained at 800° C for 3 Hrs. later on the furnace is cooled to room temperature and the carbon is collected from the Quartz boat. This obtained Carbon Nanomaterials are crushed in the form of fine powder.

The raw product (Carbon Nanomaterials) obtained was soaked in 3M HNO_3 (A.R Grade S.D. Fine Chemicals) for 3 Hrs. After soaking, the solid substance was washed several times with D.I. water and then with acetone. It was finally dried at 60° C in hot air oven for 2 Hrs. Scanning Electron Microscope (SEM) observation was conducted with FEI quanta 200, Meijo University Japan, Raman spectrum of Carbon nanomaterials prepared are taken in Meijo University Japan, The method of adsorption of methylene blue in liquid phase for specific surface area determination has been adopted. Results obtained for all the samples prepared are shown in Table-3

Hydrogen Adsorption Studies

Hydrogen adsorption measurement is done using pressure difference method. The calculation is based on the Vanderwaal's relation for ideal gases, as the pressure is low (11 Bars) we have assumed the gas is behaving like ideal gases. The adsorption is studied in the unit shown in Fig. 2. This instrument is equipped with a highly sensitive pressure gauge (Killer) with an accuracy range of 0.1 Bar.

The experiments include main three steps:

a. Leak Test : Leak age of apparatus was tested before starting each experiment. For this purpose, chamber is evacuated with vacuum pump and left over night to see whether there was any leakage. Then hydrogen gas was filled in the sample cell at the desired pressure and left over night in order to measure any decrease in the pressure, if any.

b. Blank Experiment : Blank experiments are performed to remove the error in the experiments due to adsorption of hydrogen gas by the sample cell or other contacting parts of the instruments. For this the vacuum is applied and the sample cell is heated to 150° C for 3 hrs and then cooled to room temperature. Then the chamber is filled with hydrogen at 11.0 Bars and kept at room temperature for 6 Hrs, the change

Table 2 : Name of Natural precursors selected for Pyrolysis

in the pressure of hydrogen is then measured which is noted as Δp. This decrease is very less and can be considered as error due to the apparatus and is subtracted from the original value

c. Hydrogen Adsorption Measurements : Weighed Carbon nanomaterials are kept in a copper dish and kept inside the closed chamber. Now the container is evacuated to a pressure of 10^{-1} Bars and the sample is heated up to 150^{o} C for 3 hrs to remove the previously adsorbed gases. After complete degassing the valve for the vacuum is closed and the samples are allowed to

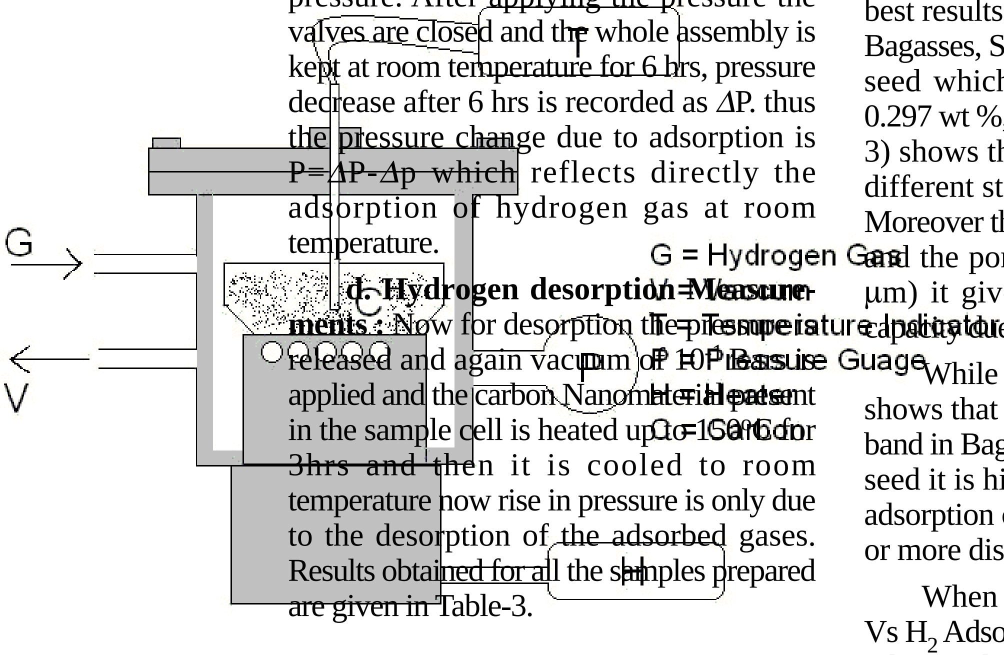


Fig. 2 : Hydrogen Adsorption Unit

cool to room temperature (30° C). Now the chamber is filled with hydrogen at 11.0 Bars pressure. After applying the pressure the valves are closed and the whole assembly is kept at room temperature for 6 hrs, pressure decrease after 6 hrs is recorded as ΔP. thus the pressure change due to adsorption is P=ΔP-Δp which reflects directly the adsorption of hydrogen gas at room temperature.

d. Hydrogen desorption Measurements : Now for desorption the pressure is released and again vacuum of 10^{-1} Bars is applied and the carbon Nanomaterial present in the sample cell is heated up to 150°C for 3hrs and then it is cooled to room temperature now rise in pressure is only due to the desorption of the adsorbed gases. Results obtained for all the samples prepared are given in Table-3.

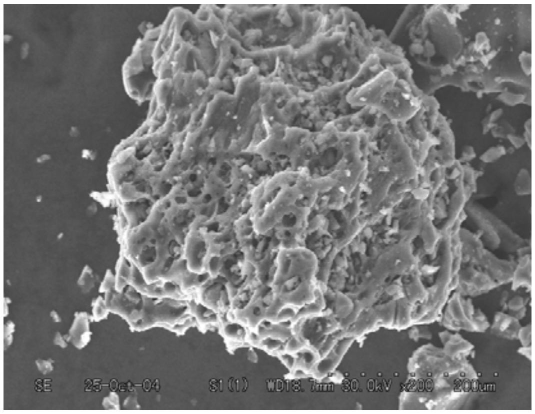
Results and Discussion

From the Table-3 it can be seen that the best results for hydrogen adsorption are of Bagasses, Soya bean, Cashew nut and Ritha seed which are 0.656, 0.599, 0.310 and 0.297 wt %, respectively. SEM images (Fig. 3) shows that Bagasses is having entirely different structure with internal channels. Moreover the particle size is big (≈ 100 μm) and the pore diameter is also large (≈ 10 μm) it gives good hydrogen adsorption capacity due to presence of internal channels.

While Raman spectra of four samples shows that the intensity of G-band and D-band in Bagasses is the lowest and for Ritha seed it is highest, this indicates the higher adsorption capacity with less intense peaks or more disordered carbon.

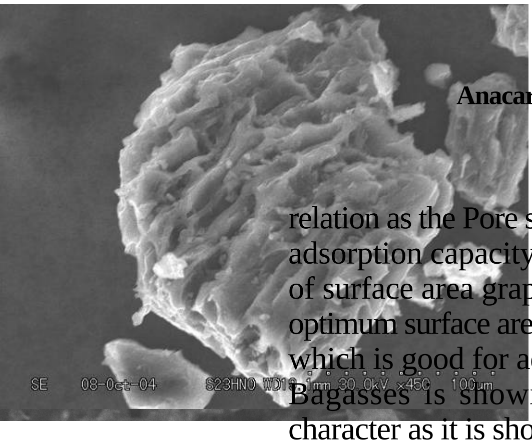
When we plot the graph of Pore Size Vs H_2 Adsorption Fig. 5(a) it shows random relation, but some of them are showing

Table 3 : Name, Density, Surface Area and Hydrogen Adsorption, Desorption Values of Prepared Carbon Nanomaterials



Soybean seeds

Bagasse fibers



Anacardium Seed

Ritha seeds

Fig. 3 : SEM micrographs

relation as the Pore size increases Hydrogen adsorption capacity decreases, but in case of surface area graph shows that there is a optimum surface area of about 60-70 m^2/gm which is good for adsorption of hydrogen. Bagasses is showing entirely different character as it is showing highest hydrogen adsorption with highest surface area and pore size is of 10.12 ìm

Taguchi Optimization Technology

To optimize the synthesis parameters we used the standard taguchi optimization technology which is based on orthogonal array and statistical calculations. Generally, a process to be optimized has several control factors, which directly decide the target or desired value of the output. The optimization then involves determining the best control factor levels so that the output is at the target value. According to the preliminary experiments the main effective parameters are considered as (A) Precursor, (B) Temperature, (C) Pre treatment, (D). The table of different parameters and their level are given below in Table 4:

Fig. 4 : RAMAN Spectra

Fig. 5 Graph of (a) Pore Size Vs H2 Adsorption

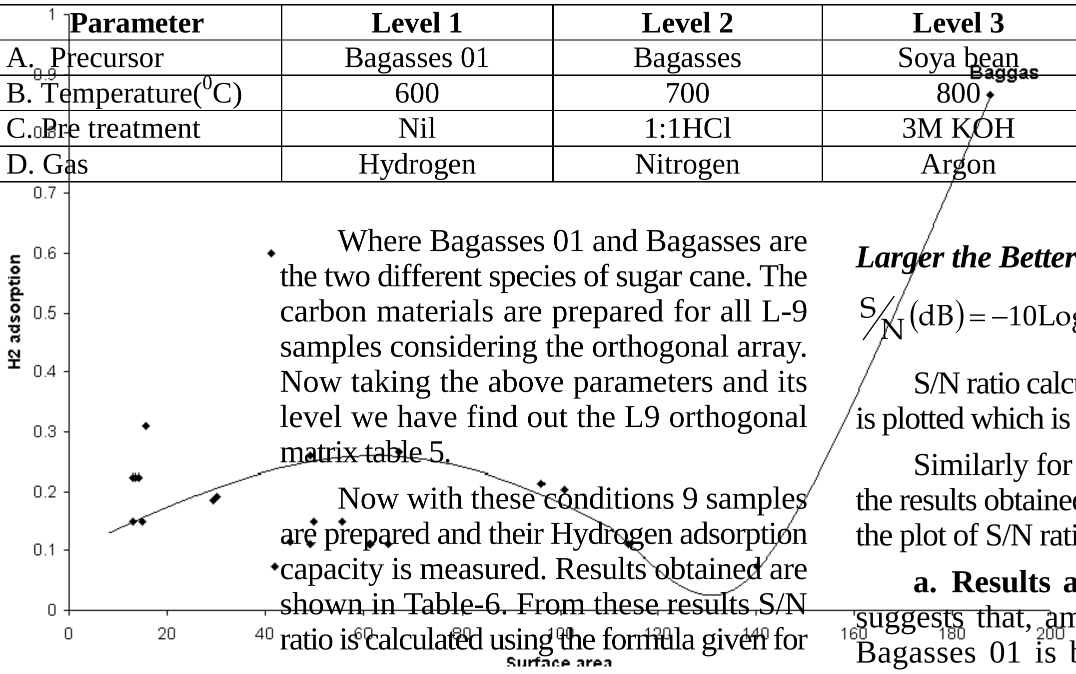


Fig. 5 Graph of (b) Surface Area Vs H2 Adsorption

Table 4 : Different parameters and its levels for L9 orthogonal matrix

Parameter	Level 1	Level 2	Level 3
A. Precursor	Bagasses 01	Bagasses	Soya bean
B. Temperature(^{0}C)	600	700	800
C. Pre treatment	Nil	1:1HCl	3M KOH
D. Gas	Hydrogen	Nitrogen	Argon

Where Bagasses 01 and Bagasses are the two different species of sugar cane. The carbon materials are prepared for all L-9 samples considering the orthogonal array. Now taking the above parameters and its level we have find out the L9 orthogonal matrix table 5.

Now with these conditions 9 samples are prepared and their Hydrogen adsorption capacity is measured. Results obtained are shown in Table-6. From these results S/N ratio is calculated using the formula given for ***Larger the Better*** results (Equation-1).

$$\frac{S}{N}(\mathrm{dB}) = -10\mathrm{Log}_{10}\left(\frac{1}{n}\right)\sum \frac{1}{y_i}^{2} \quad ......(1)$$

S/N ratio calculated for each parameters is plotted which is shown in Fig. 6

Similarly for Desorption of Hydrogen the results obtained are given in Table-7 and the plot of S/N ratio is shown in Fig. 7

a. Results and Discussion : Fig. 6 suggests that, amongst three precursors, Bagasses 01 is better. Temperatures of

Table 5 : L9 for Optimization of parameters

Exp. No.	Precursor	Temp	Pretreatment	Gas
L-1	Bagasses 01	600	Nil	Hydrogen
L-2	Bagasses 01	700	1:1HCl	Nitrogen
L-3	Bagasses 01	800	3M KOH	Argon
L-4	Bagasses	600	1:1HCl	Argon
L-5	Bagasses	700	3M KOH	Hydrogen
L-6	Bagasses	800	Nil	Nitrogen
L-7	Soya bean	600	3M KOH	Nitrogen
L-8	Soya bean	700	Nil	Argon
L-9	Soya bean	800	1:1HCl	Hydrogen

Table 6 : Hydrogen adsorption of L-9 Samples

Exp. No.	H2 Adsorption (wt %)		S/N ratio
L-1	3.98	2.01	8.088
L-2	3.18	1.20	4.015
L-3	1.59	2.20	5.213
L-4	1.61	1.19	2.628
L-5	3.42	1.92	7.846
L-6	2.42	1.61	5.555
L-7	2.20	1.60	4.014
L-8	2.03	1.98	6.040
L-9	1.99	1.18	3.139
Mean S/N ratio=			5.179

pyrolysis should be 700° C and Hydrogen adsorption is better any treatment. Finally pyrolysis in Hydrogen atmosphere is better than Nitrogen or Argon.

For getting better desorption of hydrogen, Bagasses 01 is better. Desorption is better when pyrolysis is done at 600° C. No acid treatment should be done. Surprisingly, pyrolysed product under Nitrogen gives more desorption than Hydrogen environment.

CNM synthesized with these optimized parameters i.e. with Bagasses 01 at 600° C, without any treatment and in Nitrogen atmosphere showed the hydrogen adsorption of 2.99 wt %. Thus the optimization of parameters increases the adsorption capacity up to 5 fold i.e. from 0.656 wt % to 2.99 wt %.

Activation of CNM's with metals

For still enhancing the hydrogen adsorption capacity we have decided to activate these carbon materials with metals. There are number of methods adopted by the scientist for the activation by insertion of metal in carbon skeleton, in this method the metal chloride with carbon is converted in to fine particles of metal hydroxide with the simple reaction of precipitation with ammonium hydroxide.

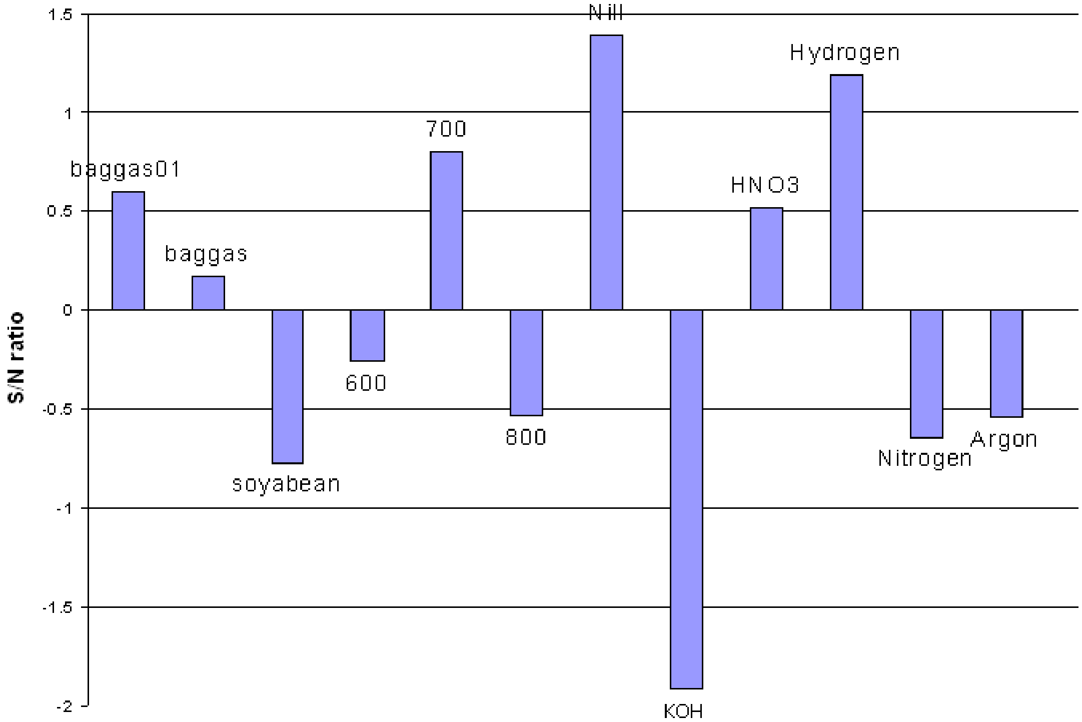


Fig. 6 : Effect of each parameter levels on hydrogen adsorption

Table 7 : Hydrogen Desorption of L-9 Samples

Exp. No.	H2 Desorption (wt %)		S/N ratio
L-1	0.39	0.39	-8.178
L-2	0.79	0.39	-6.115
L-3	0.00	0.40	0.00
L-4	0.00	0.00	0.00
L-5	0.00	0.00	0.00
L-6	0.39	0.79	-6.115
L-7	0.79	0.39	-6.115
L-8	0.00	0.00	0.00
L-9	0.00	0.00	0.00
Mean S/N ratio =			-2.947

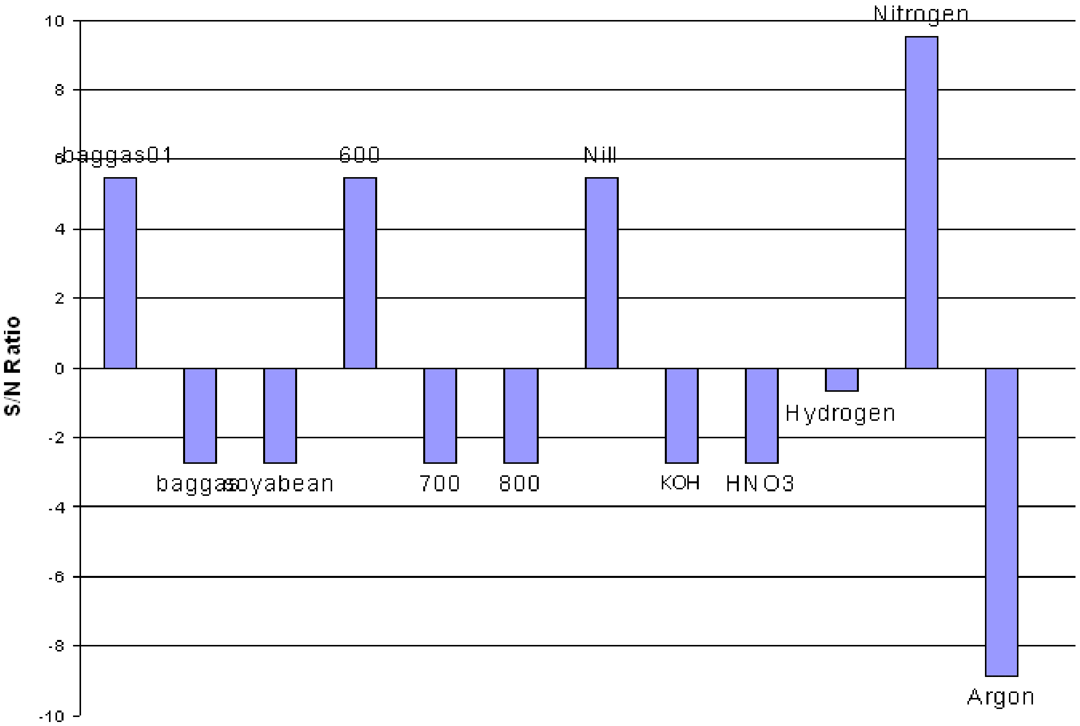


Fig. 7 : Effect of each parameter levels on hydrogen desorption

The precipitate of metal hydroxide is washed and dried. Now this dried powder is decomposed thermally at high temperature in atmosphere of Hydrogen for reduction.

This mixture will be heated in inert atmosphere of H_2 at the temperature of decomposition of metal hydroxide. At this temperature the metal hydroxide will get decomposed and is converted to metal which is inserted in carbon matrix. Prepared carbon nanomaterials with metals are studied for their Hydrogen adsorption by Seivert's method at high pressure. These samples are analysed by TEM micrograph.

b. Results and Discussion : TEM images (fig 8) show the uniform distribution of metal particles on the surface of carbon material. In case of Mn and Zn the number of particle is very less and the size is also not uniform, the average particle size of Mn and Zn are 100nm and 60nm respectively. But in case of Mg the number of particle is more and in Ni it is even higher and the average particle size goes on decreasing. But hydrogen adsorption capacity is increasing in Ni compound.

From these treatments it is clear that CNM with Ni in hydrogen gas treatment gives maximum adsorption capacity of 4.36 wt % while CNM with Mg gives adsorption capacity of 1.84 wt %.

Table 8 : Hydrogen adsorption by Severt's method

CNM soaked with metal	Temperature ^{o}C	Gas treatment	Hydrogen adsorption (w%) at 80bar pressure
CNM-Mn (2:1)	800	Hydrogen	0.415
CNM-Mg (2:1))	800	Hydrogen	1.84
CNM-Zn (2:1)	800	Hydrogen	1.098
CNM-Ni (2:1)	800	Hydrogen	4.36

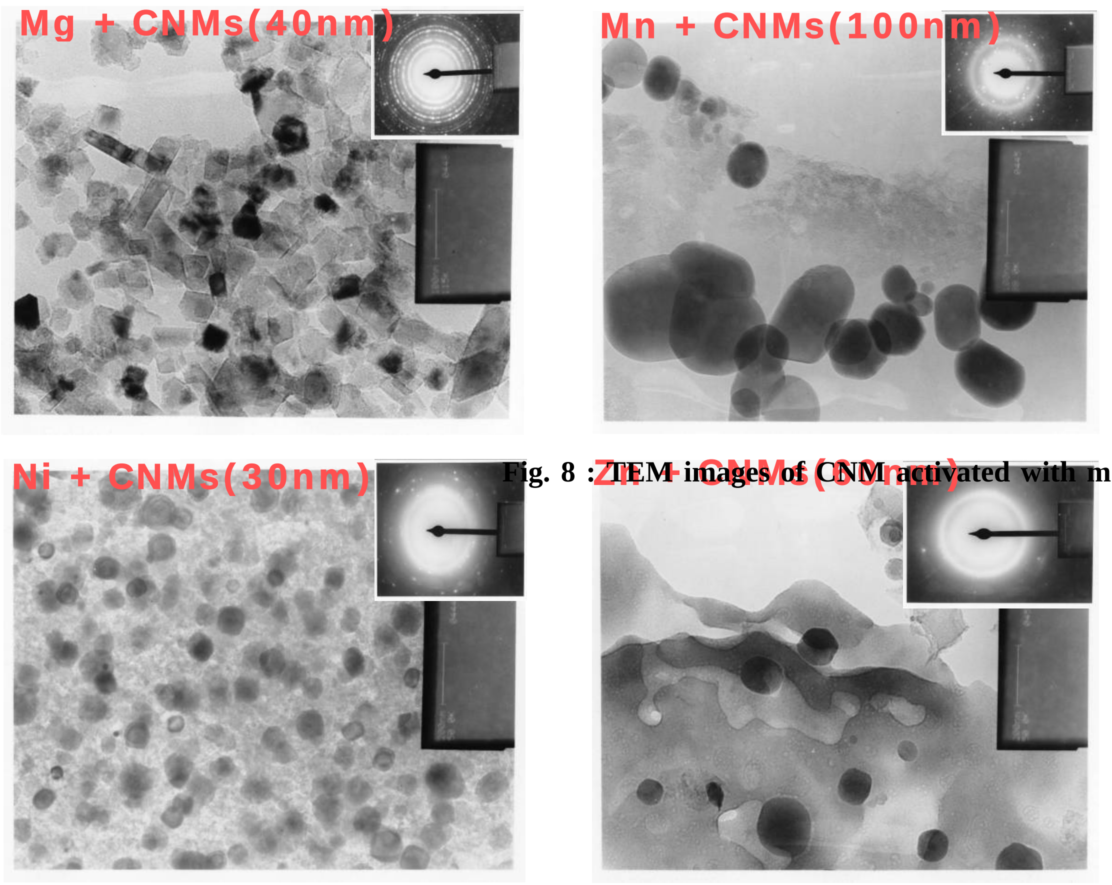


Fig. 8 : TEM images of CNM activated with metals

Conclusion

Pyrolysis of different natural precursors including oil, seed, fibers and other waste materials are done and hydrogen adsorption is measured for all the precursors. It was found that Bagasses 01 is the best precursor for the adsorption of hydrogen gas and it gives adsorption capacity of 0.656 wt %. To optimize the preparation conditions, Taguchi optimization technology is used. This resulted into 5 fold increase in hydrogen adsorption (i.e. from 0.656 wt % to 2.99 wt %). Raman Spectra gave a clearly that "Increase in graphitic character decreases the hydrogen adsorption capacity" and the highly ordered arrangement of carbon is not required for high hydrogen capacity. When this carbon Nanomaterial is activated with Ni nanoparticles hydrogen adsorption capacity increases up to 4.36 wt %.

References

Herold A. (1955) : Bull. Soc. Chim. France **197,** 999.

Dillon A.C., Jones K.M., Bekkedahl T.A., Kiang C.H., Bethume D.S. and Heben M.J.(1997) : *Nature,* **386(27),** 377-91.

Chattarjee A. K., Maheshwar Sharon, Ranjan Bannerjee, Michael Neumann Spallart (2003) : *Electrochimica Acta,* **48**, 3439-3446.

Kaewprasit C. (1998) : Eric Hequet; *The Journal of Cotton Science,* **2,** 164-173.

Isihara T. (2000) : Ahira fukunaga, Ranko akiyoshi, Masaki yoshio, Yusaku takita, *Electrochemistry,* **68(1)**, 38-41.

Wang C., Kakwan I., Appleby A. John, Frank E. Little J. (2000) of *electroanalytical chemistry,* **489,** 55-67.

Frackowiak E , Delpeux S., Jurewicz K., Szostak K., Cazorla A., Beeguin F. (2002) : *Chemical Physics Letters*, **361**, 35.

Aves G.D., Berry G.D., (1998) : Rambach. *Int J. Hydrogen Energy*, **23(7),** 583-91.

Ijima S. Nature (London) 1991, 354, 56.

Jaeyun Kim, Jinwoo Lee, Taeghwan Hyeon (2004) : *Carbon*, 42, 2711–2719

Li Zhou, Yaping Zhou and Yan Sun (2006) : *International Journal of Hydrogen Energy*, **31(2)**, 259-264.

M. Sharon, W. K.Hsu, H. W. Kroto, D. R. M. Walton, A. Kawahara, T. Ishihara, Y. Takita. J. of Power Sources 104 (2002) 148-153M. Sharon

M.Winter, J.O.Besenhard in book "Lithium ion batteries-Fundamental and performance" Kodansha Scintific Ltd., Tokyo, Wiley-VCH, Weinheim(1998)p 127-155.

Maheshwar Sharon, Mukul kumar, P.D. Kichambare, Yoshinori Ando and Xinlus Zhao Diamond Film & Tech. **8(3),** 1998.

Pradhan D., Sharon M., Material Science and Engineering 2002, B 96, 24.

S. Wang, S.Yata, J.Nagano, Y.Okano, H.Kinoshita, H.Kikuta, T.Yamabe, The Electrochemical Society. 147 (2000) 2498-2502.

S.H.Ng, J.Wang, Z.P.Guo, J.Chen, G.X.Wang, H.K.Liu. Electrochemica acta 51(2005)23-28

Stuart S, J. Barton J, Carbon 1987; 25(3) p 343-350

T. Hirai, 1. Yoshimatsu, J. Yamaki, J. Electrochem. Soc. 141 (1994) 2300.

V.R. Koch, J.L. Goldman, C.J. Mattos, M. Mulvaney, J. Electrochem. Soc. 129 (1982).

Yu-Run Lin and Hsisheng Teng Microporous and Mesoporous Materials, Volume 54, Issues 1-2, 1 July 2002, Pages 167-174