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Microwave Assisted Synthesis of Activated Carbon Fibers from Silk Cotton

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Abstract: Water pollution due to the discharge of untreated effluents increases every day. The technologies available at present are either ineffective for wide variety of pollutants or the operational cost is high. Search of a technology which can overcome these limitations is highly warranted in the present context. Adsorption using activated materials is a convincing technology, but the precursor for the preparation of activated carbon should be renewable, low cost and should have superior surface characteristics. In this analysis high surface activated carbon fibers were synthesized from silk cotton (widely available and renewable low cost material). Two stage microwave synthesis produces a carbon fiber with surface area of 1041.08 m^2/g and a total pore volume of 0.4944 cm^3/g. The microwave synthesis gives a carbon fiber with excellent porosity and produces rose flower like activated carbon as shown in the SEM images. FTIR spectroscopic studies substantiates that microwave heating is very effective for the removal of surface functionalities and there by makes a universal adsorbent fiber.
Keywords: Adsorption, Surface Area, Porosity, Activation, Pyrolysis.

1.0 Introduction

The pollution of the environment increases day by day due to the discharge of non-degradable and hazardous compounds. The major sources of these pollutants are the untreated effluents released from various industries. Many industries like paper, printing, textile finishing etc use dyes to impart colour to their products and consume large volume of water. As a result, these industries generate large volume of coloured wastewater. Especially in dyeing industry effluents presence of very small amounts of (some cases less than 1 mg/L) dye molecules produces obvious water coloration. The presence of dye molecules not only toxic but they also reduces the penetration of light there by retards the growth of aquatic organisms.

Many technologies are available in the present context are either costly or not effective for all classes of pollutants. In addition, the textile dyeing industries are facing increasing pressure from the environmental regulatory boards to replace the conventional treatment technologies with eco friendly one. Adsorption using activated materials is one of the most effective methods for the removal of wide range of pollutants. Activated carbon is one of the most preferred adsorbent over other adsorbents due to its high surface area, easy availability etc. However, the high operating cost and difficulties in regeneration of activated carbon leads to many researchers to search for more economic adsorbents. Use of biomass consisting mainly of agricultural and forestry waste, can be regarded as a renewable energy source with great potential to supply the global material demands. Moreover, the use of biomass contributes to reduce the greenhouse effect. The candidature for a low cost adsorbent should have the qualities like cheap, easy availability and disposable without regeneration.

Biological waste materials like coconut shells[1] walnut shell[2], bagasses[3,4], peat moss[5], coir pith[6,7], corncob[8], plum kernels[9], pinewood[10], fir wood[11], rice husk[12], lignin[13] etc., have been tried successfully in the past as a low cost adsorbent.

Microwave heating is one of the most versatile methodologies for the preparation of activated carbon. The basics of microwave heating are the dielectric heating in which energy is absorbed by ions or molecules that are either induced or permanent dipoles. Unlike conventional heating, the energy conversion occurs by two mechanisms: ion conduction and dipole rotation inside particles[14,15]. In the Microwave carbonization process, the efficiency is very close to 100, i.e. almost the carbon from biomass is converted into carbonized material, without generating CO and CO_2[16].

Microwave assisted hydrothermal carbonization is one of the most advanced technologies to convert biomass and waste with high moisture levels, because it eliminates the drying step. In addition, hydrothermal carbonization efficiently decomposes the carbohydrates in biomass, such as cellulose and hemi-cellulose by hydrolysis, to produce sugars and other decomposition byproducts, i.e. organic acids and aldehydes[17,18]. Microwave heating has been used to prepare activated carbon using pine apple peel, tobacco stem, rice husk, mangosteen peel, cotton stalks, and orange peel precursors[19-22].

In the present work silk cotton fiber is used as a precursor for the preparation of highly porous activated carbon using microwave hydrothermal process. About the precursor (silk cotton fiber) is available in plenty in countries like India and some parts of Asia. The advantage of the precursor is not only available in plenty also it is renewable with short span of time with very good yield.

2.0 Experimental

All the chemicals used for the study are analytical grade reagents supplied by Aldrich-India (>99 % purity). Double distilled water is used as a solvent as well as for all dilutions.

2.1 Preparation of Activated Carbon Fibers

2.1.1 Simple pyrolysis with muffle furnace (C1)

The precursor (Silk cotton fiber) was soaked with 0.5% (W/V) solution of $FeCl_3$ for one hour. After one hour of impregnation, the fibers were removed from the solution and air dried for 24 hours. The air dried sample was carbonized in Muffle furnace at 600 °C for 20 min. The carbon was washed with plenty of water to remove any residual chemicals. The washed carbon dried in hot air oven at 110°C for 24 hrs. Finally the dried carbon activated in N_2 atmosphere at 800°C for 10 min, labeled as C_1 and stored in tight lid container for further studies.

2.1.2 Carbonization by pyrolysis followed by microwave activation (C2)

The precursor was soaked with 0.5% (W/V) solution of $FeCl_3$ for one hour. After one hour of impregnation, the fibers were removed from the solution and air dried for 24 hours. The air dried sample was carbonized in Muffle furnace at 600 °C for 20 min. The carbon was washed with plenty of water to remove any residual chemicals. The washed carbon activated in microwave oven in N_2 atmosphere at 600w for 10 min, labeled as C_2 and stored in tight lid container for further studies.

2.1.3 Carbonization by microwave followed by muffle furnace activation (C3)

The precursor was soaked with 0.5% (W/V) solution of $FeCl_3$ for one hour. After one hour of impregnation, the fibers were removed from the solution and carbonized in microwave oven at 600w for 05 min. The carbon wass washed with plenty of water to remove any residual chemicals. The washed carbon activated in muffle furnace in N_2 atmosphere at 800°C for 10 min, labeled as C_3 and stored in tight lid container for further studies.

2.1.4 Carbonization and by microwave heating (C4)

The precursor was soaked with 0.5% (W/V) solution of $FeCl_3$ for one hour. After one hour of impregnation, the fibers were removed from the solution and carbonized in microwave oven at 600w for 05 min. The carbon was washed with plenty of water to remove any residual chemicals. The washed carbon activated in microwave oven in N_2 atmosphere at 600w for 10 min, labeled as C_4 and stored in tight lid container for further studies.

3.0 Results and Discussion

The physico chemical and textural properties of the four different activated carbon fibers are given in table 1. The activated carbon prepared using simple thermal pyrolysis shows poor development of porosity with BET surface area of 360.42 m^2/g. The pore volume of C1 also found to be lowest among all the four variant of carbons. When conventional pyrolysis alone used, either the porosity development is poor or higher temperature could have destroyed a part of developed micropores and mesopores.

Table 1 - Surface characteristics of the activated carbon fibers.

S.No.	Parameters	Carbon Fiber			
		C1	C2	C3	C4
1.	S_{BET} (m^2/g)	360.42	774.52	805.87	1041.08
2.	$S_{Langmuir}$(m^2/g)	408.37	869.37	1099.67	1502.71
3.	$S_{ext.}$ (m^2/g)	100.77	404.86	411.48	281.52
4.	Total pore surface area (m^2/g)	396.39	806.14	884.12	1327.45
5.	Total volume (cm^3/g)	0.2716	0.3749	0.4141	0.4944
6.	Micropore area (m^2/g)	216.74	591.11	688.18	771.61
7.	Mesopore area (m^2/g)	96.42	100.64	195.82	155.22
8.	Micropore volume (cm^3/g)	0.1336	0.2763	0.1778	0.3411
9.	Mesopore volume (cm^3/g)	0.0976	0.1135	0.1181	0.1791
10.	Average pore diameter (nm)	2.11	2.24	2.16	2.09
11.	Iodine number (mg/g)	296.70	719.56	443.12	565.06
12.	pH_{zpc}	5.96	6.14	6.63	5.05
13.	Density (g/cm^3)	0.44	0.46	0.41	0.49
14.	Yield (%)	50.45	48.16	48.01	47.71

When conventional heating coupled with microware heating, the porosity development was slightly improved. The carbon C2 prepared by carbonizing the silk cotton using conventional heating followed by activation using microwave. This process produces an activated carbon with a BET surface area of 774.52 m^2/g and a pore volume of 0.3749 cm^3/g. The combined heating method slightly improves the development of porosity. Initial pyrolysis makes the exit of all Volatile Organic Compounds (VOC) and other volatile compounds. In the second stage the carbon subjected to microwave irradiation, the interaction of microwave with the matters present in the carbon is not effective. As the microwave heating is based on dielectric heating in which energy is absorbed by ions or molecules that are either induced or permanent dipoles. Majority of the microwave energy is transmitted to the molecule in the form of dipole rotation inside the particle[14,15]. Where as the activation of carbon using microwave irradiation produces a marginal influence on the porosity development.

In the third method the precursor along with Fe catalyst first exposed to microwave irradiation followed by activation using conventional muffle furnace heating. This scheme of heating yielded a good result with well developed carbon fibers. During initial heating the $FeCl_3$ decomposes and produces nano-iron which favors the formation of well developed porous carbon and also nano-iron favors the complete removal of all volatile compounds. Rodriguez and Mendez have prepared different activated carbons with iron hydro(oxide) nano-particles and it was tested for its ability to absorb arsenic from water[23]. When the initial heating is carried out with microwave source, it produces homogeneous and quick heating at molecular level leading to the formation of clean char. The second stage of third scheme is conventional pyrolysis. This stage along with first stage microwave heating produces an activated carbon with a surface area of 805.87 m^2/g and a pore volume of 0.4141 cm^3/g. While analyzing the second and third scheme of combined heating the microwave heating is more efficient than conventional pyrolysis.

Based on the above findings another sequence of heating tested by microwave for both carbonization and activation steps. Among the microwave active material, carbons are in general, good microwave active and they can be easily transformed by microwave heating. Recently many researchers are working towards the development of highly active and porous carbon using microwave irradiation. The carbon C4 prepared using microwave carbonization as well as microwave activation found to have excellent porosity and high surface area. The carbon C4 has a BET surface area of 1041.08 m^2/g and a total pore volume of 0.4944 cm^3/g. In the case of solid dielectric material with charged particles which are free to move in a delimited region of the

material, such as π-electrons in a carbon materials, a current traveling in phase with electromagnetic field is induced[24]. As the electrons cannot couple to the changes of phase of the electric field, energy is dissipated in the form of heat due to the so called Maxwell-Wagner (Interfacial or Maxwell-Wagner polarization) effect[25,26].

The above said combined effect in the forth sequence produces an excellent adsorbent with an exceptionally developed porous surface structure. During carbonization the raise of material could have occurred very rapidly during microwave heating, which enhances the porosity development. The surface area and pore volume of the carbon C4 found to be comparable with the results reported by some of the previous researchers[27-29].

3.1 FTIR Studies

Infrared spectroscopic analysis was carried out to obtain information about the chemical structure and functional groups of the prepared activated carbons. As shown in fig. 1, the different heating schemes have a different role in the removal of various functionalities present on the surface of activated carbon. All the four carbons have a broad peak around 3600 to 3700 cm^{-1} corresponds to the O-H stretching vibration of the hydroxyl functional groups including hydrogen bonding. The C-H stretching vibrations in all the four carbons was found at 3000 to 3050 cm^{-1}. These peaks were ascertained for the symmetric and asymmetric stretching vibrations of ethyl and methylene groups[29]. The C-H stretching peaks slowly disappeared in C4 which indicates the high charring capacity and effective carbonization by microwave heating.

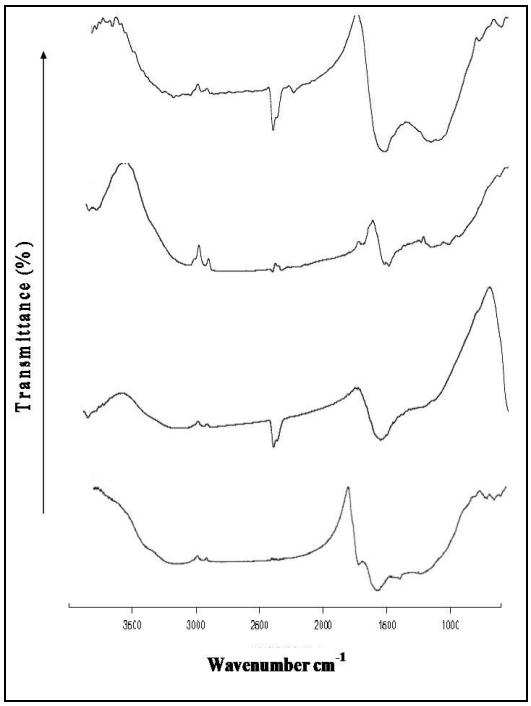

Figure 1 – FTIR spectrum of activated carbon fiber

The C-C stretching vibrations occurred around 2200 to2350 cm^{-1} observed in C1, C2 and C3, where as it was disappeared in C4. This is due to the violent pyrolytic reaction of char by microwave heating. All the four activated carbons show strong and broad peak at 1500 to 1600 cm^{-1} indicates high amount of unsaturation. After the volatilization a completely fused aromatic system would have resulted by microwave heating. During the preparation of an activated carbon, microwave heating has mainly been used for the rapid elimination of surface functionalities that are often present on the carbon surface. The microwave heating has been used to remove oxygen functionalities and produce activated carbon in few minutes[30]. Another peak around 1100 to 1150 cm^{-1} related to C-O stretching vibrations of alcoholic, phenolic and carboxylic groups were present in C1, C2 and C3 but the peak disappears in C4. The peaks related to out-of-plane bending vibrations of O-H was clearly observed in C4 which depicts that the highly porous C4 carbon will have the normal tendency to adsorb atmospheric H_2O which results in the respective peak.

3.2 SEM Analysis

The scanning electron microscopic images of the prepared carbon fibers were given in fig. 2 to 5. The SEM images of C1 (figure 2) indicates that the carbon fibers were found with a diameter of 1 to 5 μm. The surfaces of the carbon fibers were clean and smooth. The development of rough surface and porosity in C1 is not up to the level of a good adsorbent. In C2 (figure 3) carbon the introduction of microwave heating during activation leads to the formation of highly fragmented carbon fiber. An appreciable amount of rough surface and ridges were created in the carbon surface. On analyzing the SEM images of C3 carbon fibers (figure 4) with hollow structures were observed. This type of hollow fiber formation could have been indicated in the carbonization step using microwave.

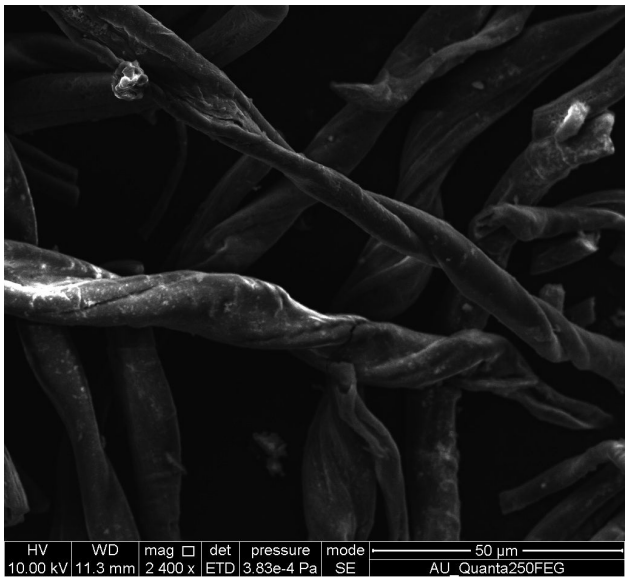

Figure 2 – SEM image of C1

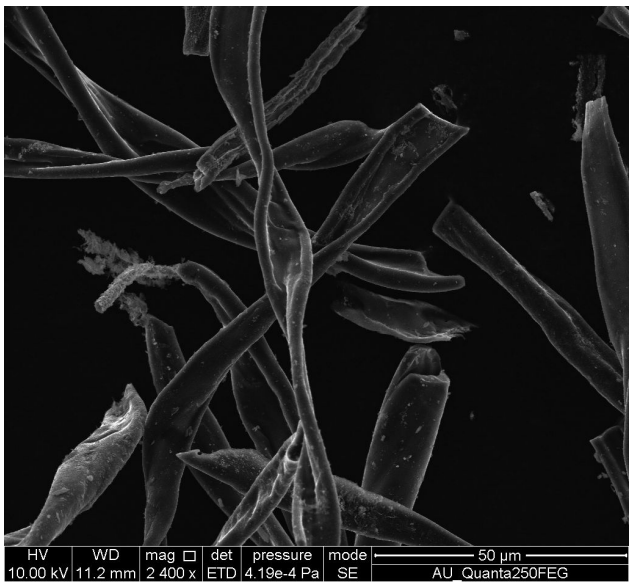

Figure 3 – SEM image of C2

Two stage microwave irradiation of silk cotton fiber along with $FeCl_3$ catalyst produces flower like highly porous three dimensional carbon structure. Well developed pores and great amount of roughness were observed in the SEM images of C4 (figure 5). The well developed porosity and high surface area is supported by the BET surface area and total pore volume. The rose flower like activated carbon fiber could be capable of removing good amount of pollutants in wastewater.

Figure 4 – SEM image of C3

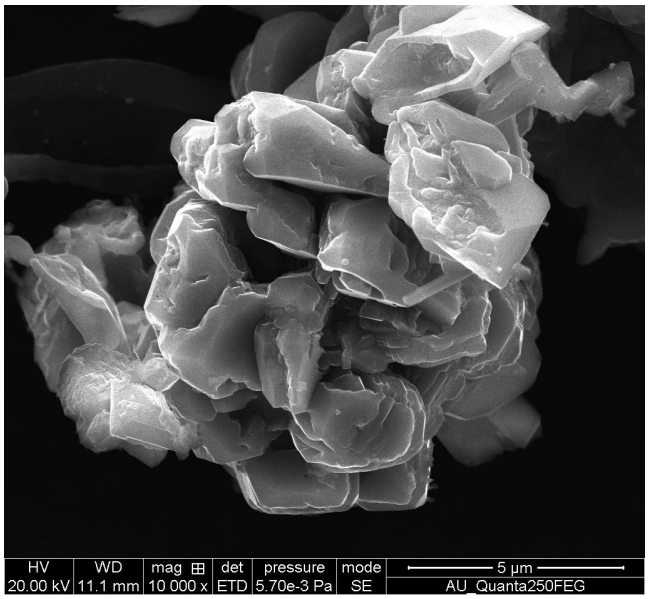

Figure 5 – SEM image of C4

The Iodine value calculated for the carbons indicates that C4 has high iodine value than other carbons. The iodine value is an indication of the ability of an adsorbent to remove small pollutant molecules. The carbon C4 truly has the adsorption capacity towards large organic molecules and metal ions. Though the microwave irradiation produces low yield of activated carbon, the other surface characteristics which are essential for an activated carbon are much better than C1, C2 and C3.

4.0 Conclusions

Activated carbon fibers with excellent surface characteristics were conveniently and economically prepared from silk cotton fiber using microwave heating technology. Microwave heating produces an activated carbon fiber with a BET surface area of 1041.08 m^2/g and a total pore volume of 0.4944 cm^3/g. FTIR studies demonstrates that microwave heating enhances the removal of volatile matter with more efficiency than conventional thermal pyrolysis. Two stage microwave irradiation of silk cotton fiber along with $FeCl_3$ catalyst produces flower like highly porous three dimensional carbon structure. Carbon fiber prepared using microwave irradiation would be a promising adsorbent for the removal of pollutants from wastewater.

5.0 References

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