

Preparation and Characterization of Activated Henequen Fiber

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Abstract

Henequen fiber was air-stabilized, carbonized, and steam-activated to obtain high surface area activated henequen fiber (AHF). Thermal behavior of henequen fibers has been studied by TGA. The structural morphology and characteristics were observed by SEM and BET surface area measurement. The yield of AHF from natural henequen was in the range of 20~25 wt%. Mesopores (2~2.5 nm) were developed on the AHF as the activation temperature was raised up to 700°C, and the band of mesopore size distribution moved to 15~30 nm when the activation were carried out at 900°C for 30 min. The specific surface area and the total pore volume were about 1394 m²/g and 1.30 cm³/g, respectively at this activation conditions.

Keywords : Activated henequen fiber, Pore size distribution, Specific surface area

1. Introduction

Activated carbon fiber (ACF), is known as one of excellent carbon adsorbents, has been obtained from various precursors by an adequate stabilization, carbonization, and activation process. ACFs are now manufactured from regenerated cellulose (viscose rayon), phenolic resin (Kynol), polyacrylonitrile (PAN), and coal tar pitch-based fibers. Recently, new materials are sought for the production of highly effective and cheap fibrous carbon adsorbents.

Natural cellulosic fibers, such as henequen (*Agave fourcroydes*, a close relative of the sisal plant), can be processed without tension to produce flexible carbon textiles. Henequen fiber has good tensile strength, used commonly in the manufacture of textile products, environmental friendliness, and biodegradable properties. Moreover, it is readily available from natural sources at a low price. Cho et al. [1] tried to use henequen fiber as a filler of composites, and resulted in the unsuitable filler due to the poor strength caused by the existence of structural flaws. However, ACF does not need high strength and modulus. Nevertheless, there are no reports about the preparation of ACF from henequen as yet.

Therefore, the purpose of this study is preparation and characterization of AHF from natural henequen fiber to investigate the production of new carbon adsorbent. To obtain the purpose: i) natural henequen fiber was stabilized, carbonized, and activated at various conditions, ii) surface morphology and properties of AHFs were investigated by EA, TGA, BET, SEM, and iii) adsorption capacity of AHFs was evaluated by removal of contaminants from aqueous water.

2. Experimental

2.1. Materials

Refined henequen fibers (*Agave fourcroyde*), originated from Mexico, were supplied by KRICT research center. The fibers were washed with distilled water for 24 h at 25°C and dried at 60°C in a convectional oven for 24 h. It is composed of approximately 77% cellulose, 4~8% hemicelluloses, 13% lignin, 2~6% pectin and waxes by weight [2].

2.2. Preparation of activated henequen fiber

Henequen fibers were cut into small pieces (5 cm length), stabilized, carbonized, and activated. Stabilization was carried out in a box furnace at 200, 250, 270, 300, and 400°C in air. The heating rate from room temperature was 2°C/min and the temperature was held at the target temperature for required minutes. The stabilized henequen fibers (270°C, 2 hr) were subsequently carbonized at 500, 600, 700, 800, 900, and 1000°C in nitrogen condition. The heating rate from room temperature was 10°C/min. The carbonized henequen fibers (800°C, 1 hr) were activated under continuous 0.45 H₂O / N₂ (v/v) flow, in a conventional tubular furnace at 600, 700, 800, and 900°C.

2.3. Characterization

Weight loss was measured by using TGA (TGA 2050, TA Instruments, USA) to investigate the degradation of henequen and select the stabilization conditions as increasing the

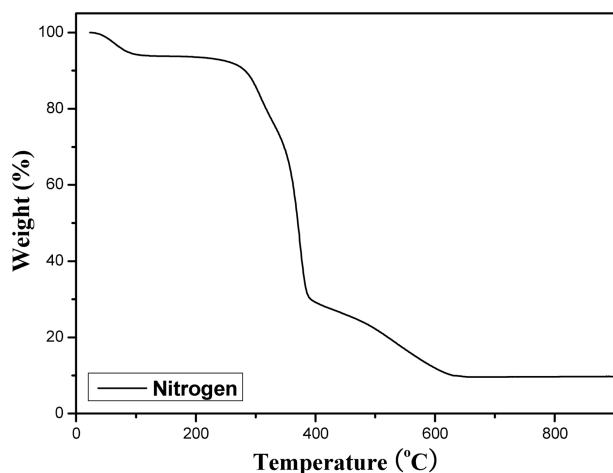


Fig. 1. TGA curve of the as-received henequen fiber in N_2 .

temperature in nitrogen surrounding. Element analysis was carried out during the stabilization and carbonization by using an elemental analyzer (Flash EA 1112, Thermo Fisher Scientific, USA). The surface morphology was observed by scanning electron microscope (SEM, JSM 5400, Japan). The adsorption characteristics of the AHFs were determined by N_2 adsorption isotherms at 77 K (Micromeritics, ASAP-2010). The surface area was calculated by the BET method. The pore volume, pore size distribution, and the average pore diameter were obtained by density function theory [3]. Methylene blue decolorization capacity was investigated by immersing 0.1 g of AHF in 100 ml aqueous solution containing 600 ppm methylene blue.

3. Results and Discussion

3.1. Stabilization

Fig. 1 shows the TGA curve of the as-received henequen fiber in nitrogen condition. About 5% weight loss under 100°C was due to the evaporation of water, and thermal degradation was rapidly progressed above 300°C. Detailed mechanism for the complete conversion of as-received henequen fiber was first presented by Bacon and Tang [4]. They reported the major thermal decomposition took place between 210 and 320°C with an ultimate weight loss of about 90%. However, the weight loss varied with 70~90%, depending on the raw materials and the rate of heating. The major part of the thermal degradation resulted from thermal cleavages of C-O and C-C linkages above 240°C and those cleavages leads to formation of large amounts of tar, H_2O , CO, and CO_2 until the temperature reached to 400°C. Nam and Netravali reported that the degradation of hemicellulose occurred between 220 and 280°C, and lignin degrades between 280 and 300°C [5]. For henequen, the major weight loss was about 70% at 400°C and more loss

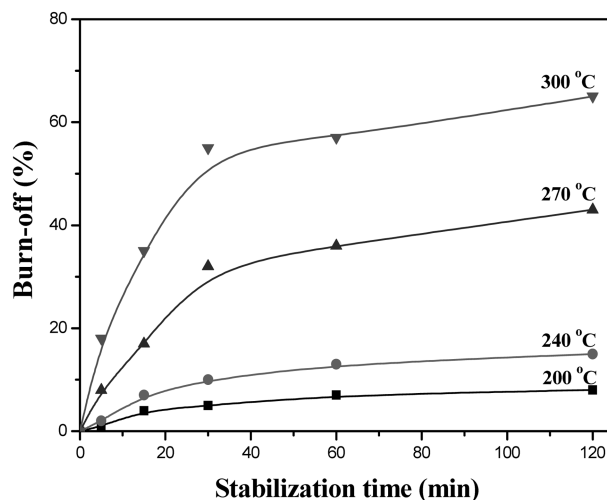


Fig. 2. Weight loss of henequen fiber as functions of stabilization time and temperatures: 200, (b) 240, (c) 270, and (d) 300°C.

Table 1. Elemental Analysis of the As-received and Stabilized Henequen Fiber (wt %)

Stabilization (°C, min.)	Carbon	Hydrogen	Oxygen	Others	C/H
As-received	43.6	6.0	45.7	4.7	0.6
200, 120	44.1	6.0	45.2	4.7	0.6
270, 120	54.8	3.9	35.9	5.4	1.2
300, 30	60.1	3.1	31.3	5.5	1.6

was carried out until 600°C, due to the evacuation of tar and gases. To obtain a C-C linked fiber, henequen fiber was air-stabilized at various stabilization temperatures and time. Fig. 2 shows the weight loss of henequen fiber as a function of stabilization temperature and time.

The weight loss was under 15% at 240°C for 2 hr. On the other hand, the weight loss was very fast in the beginning of 270°C stabilization and became slow afterward. The weight loss became faster as increasing the stabilization temperature. With these results, the optimum stabilization condition can be selected depending on weight loss. In this study, 270°C for 2 hr and 300°C for 20 min. were selected (40% weight loss) as a stabilization condition and elemental analysis, and SEM observation were carried out to investigate surface chemical constitution and morphology of the air-stabilized fiber.

Table 1 shows the elemental analysis of the as-received and stabilized henequen fibers. Carbon content gradually increased as increasing the stabilization temperature from 43.6% of the as received fiber to 60.1% of stabilized fiber at 300°C, resulting in the increase of C/H from 0.6 to 1.6, while hydrogen and oxygen content distinctly decreased due to the thermal cleavage of C-O to C-C linkage. Yue *et al.* [6] reported that the C/H molar ratio was 0.14 when they

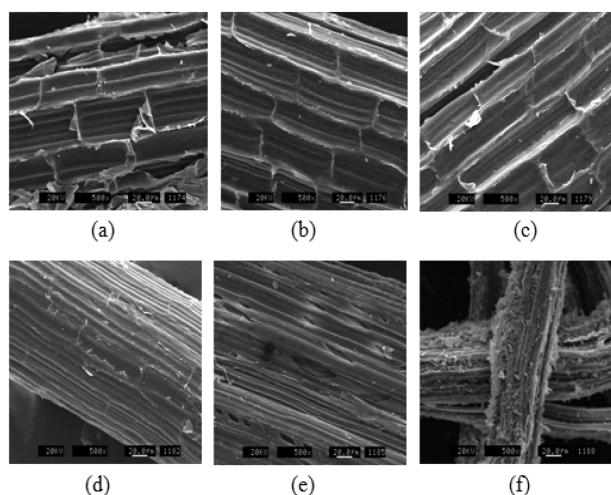


Fig. 3. SEM images of henequen fibers : (a) the as-received, and stabilized at (b) 200, (c) 240, (d) 270, (e) 300, and (f) 400°C in air.

stabilized henequen fiber at 270°C for 2 hr, which was far less than that of the results reported in this study. The difference might be come from different treatment of raw material and heating rate. In general, the weight of synthetic fibers such as polyacrylonitrile (PAN) increased due to the development of oxygen functional groups during the air stabilization [7].

Fig. 3 shows SEM images of henequen fibers. The fibrillar nature of the fibers is clearly shown. It was difficult to distinguish the surface change of fiber between the as-received fiber and stabilized fiber at 300°C, but the surface morphology of the stabilized fiber at 400°C was quite different from those of the others, due to the degradation of cell structure. These results indicated that air-stabilization should be performed lower than 300°C to maintain the fiber structure. Moreover, the treatment produces a number of small voids on the surface of the fiber that promote mechanical interlocking between the fiber and the matrix [8].

3.2. Carbonization

Fig. 5 shows burn-offs of stabilized henequen fiber (270°C, 2 hr) as a function of carbonization time and temperature in nitrogen condition. The burn-off levels rapidly increased at the beginning of carbonization up to 30 min for all the temperatures, and then slowly increased for further carbonization, resulting in the production of CO₂ and CO. It is known that CO₂ is mainly produced in the range of 300~700°C and CO is mainly produced in the range of 500~700°C, followed almost all CO over 1000°C [9]. The rapid weight loss was due to the rapid pyrolysis of cellulose fiber, because the fiber was stabilized at 270°C and put suddenly into such high carbonization temperatures. Bacon and Tang [4] reported that each cellulose unit breaks down into a residues containing four carbon atoms in this stage,

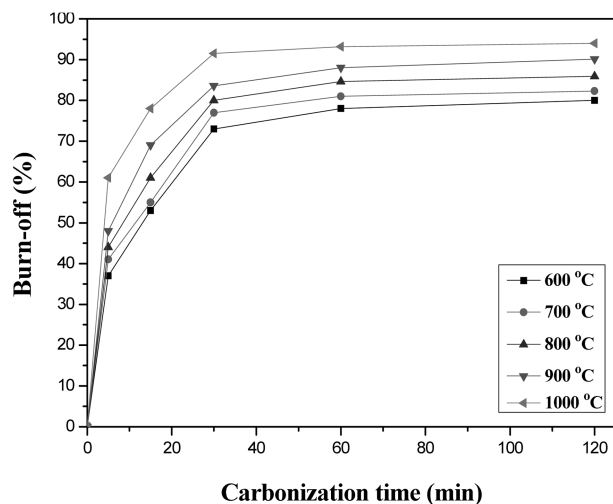


Fig. 5. Burn-offs of stabilized henequen fiber (270°C, 2 hr) as a function of carbonization time and temperature.

Table 2. Elemental Analysis of the Carbonized Henequen Fiber (wt%)

Carbonization Temp. (°C)	Carbon	Hydrogen	Oxygen	Others
600	81.1	2.1	4.8	12.0
700	81.9	1.0	4.8	13.1
800	84.9	0.1	1.0	14.0

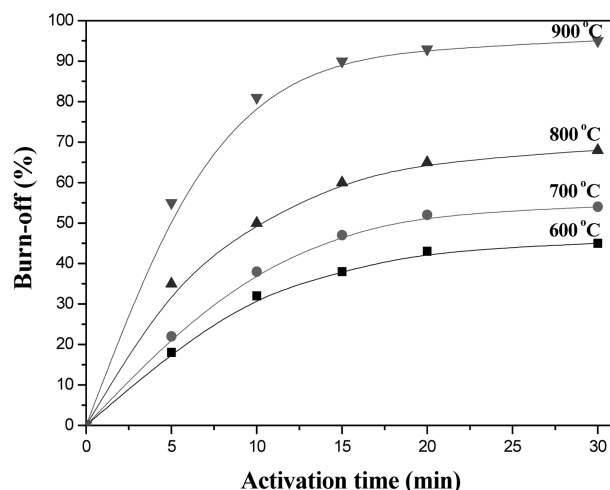


Fig. 6. Burn-offs of carbonized henequen fibers (800°C, 1 hr) as a function of activation temperature in the stream of 0.45 H₂O/N₂ (v/v).

which then repolymerize into a carbon polymer, ultimately producing a graphite-like structure above 600°C by condensation reactions involving the removal of hydrogen.

Table 2 shows elemental analysis of the carbonized henequen fiber. As expected, the carbon content gradually increased as a function of carbonization temperature. The oxygen content of the fiber carbonized at 800°C is

Table 3. Structural Characteristics of AHFs Analyzed from Nitrogen Adsorption Isotherms

Activation conditions		Properties				
Temp. (°C)	Time (min)	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D_{pore} (Å)
600	5	517	0.207	0.203	0.004	16.427
	10	573	0.229	0.221	0.008	16.635
	15	584	0.257	0.240	0.017	16.704
	20	598	0.272	0.252	0.020	17.126
	30	639	0.273	0.249	0.024	17.341
700	5	679	0.327	0.322	0.005	17.704
	10	697	0.390	0.354	0.036	20.879
	15	736	0.408	0.365	0.043	22.336
	20	782	0.445	0.393	0.052	22.478
	30	845	0.453	0.372	0.081	25.045
800	5	718	0.352	0.285	0.067	19.642
	10	808	0.441	0.343	0.098	21.834
	15	901	0.548	0.409	0.139	24.343
	20	1120	1.031	0.593	0.438	31.247
	30	1320	1.122	0.518	0.604	40.061
900	5	853	0.416	0.307	0.109	20.737
	10	929	0.525	0.335	0.190	22.614
	15	1022	0.652	0.385	0.267	25.518
	20	1254	1.115	0.540	0.475	32.365
	30	1394	1.309	0.471	0.838	40.216

significantly smaller than that of the other fibers carbonized at lower temperatures, while Prauchner *et al.* [10] reported that aromatic rings start to undergo condensation above 700°C resulting in the formation of micropores during carbonization.

3.3. Activation

Fig. 6 shows burn-offs of carbonized henequen fibers (800°C, 1 hr) as a function of activation temperature at 600, 700, 800 and 900°C in the stream of 0.45 $\text{H}_2\text{O}/\text{N}_2$ (v/v). The burn-offs gradually increased with the increase of activation temperature, and that of the fiber carbonized at 900°C was significantly increased due to the higher activation temperature than carbonization temperature. Therefore, proper AHF can be chosen from the measurements of adsorption isotherms, specific surface area, and pore size distribution.

Table 3 shows structural characteristics of AHFs analyzed from nitrogen adsorption isotherms. The BET specific surface area, pore volume, and pore diameter increased as activation temperature and time increased. Especially micropore volume gradually increased up to 20 min, which resulted in the increase of specific surface area. On the other hand, micropore volumes decreased, while mesopore volumes continuously increased with more than 20 min activation.

Fig. 7 shows nitrogen adsorption and desorption isotherms

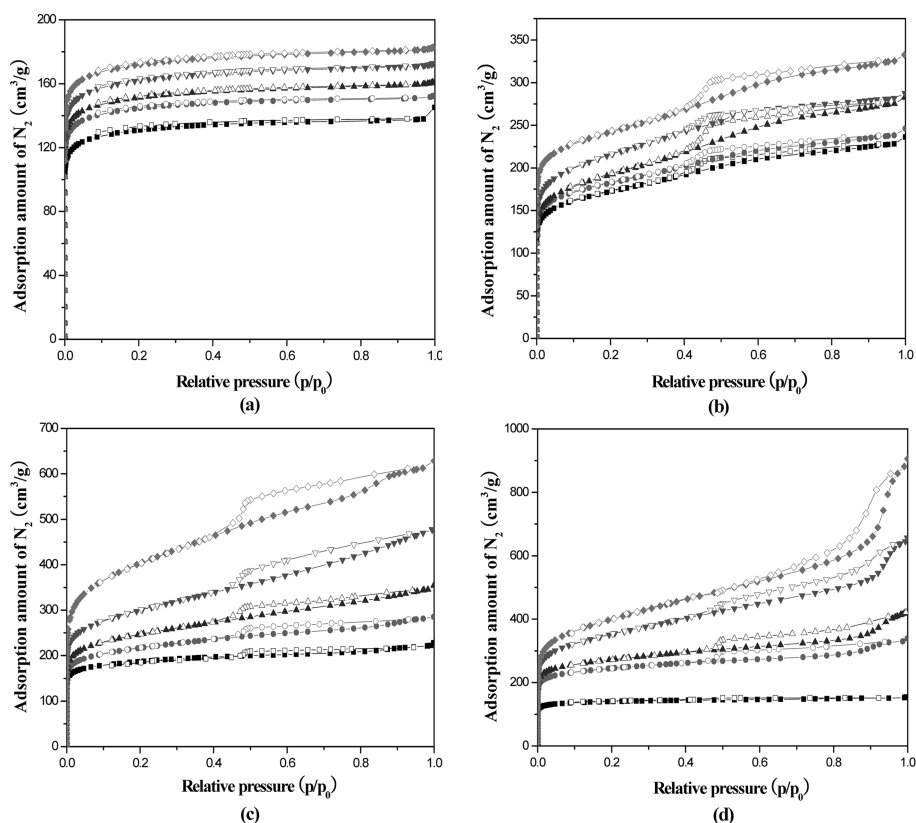


Fig. 7. Nitrogen adsorption isotherms of AHFs prepared at different temp. : (a) 600, (b) 700, (c) 800, and (d) 900°C and time : □-5, ○-10, △-15, ▽-20, and ◇-30 min (solid = adsorption, open = desorption).

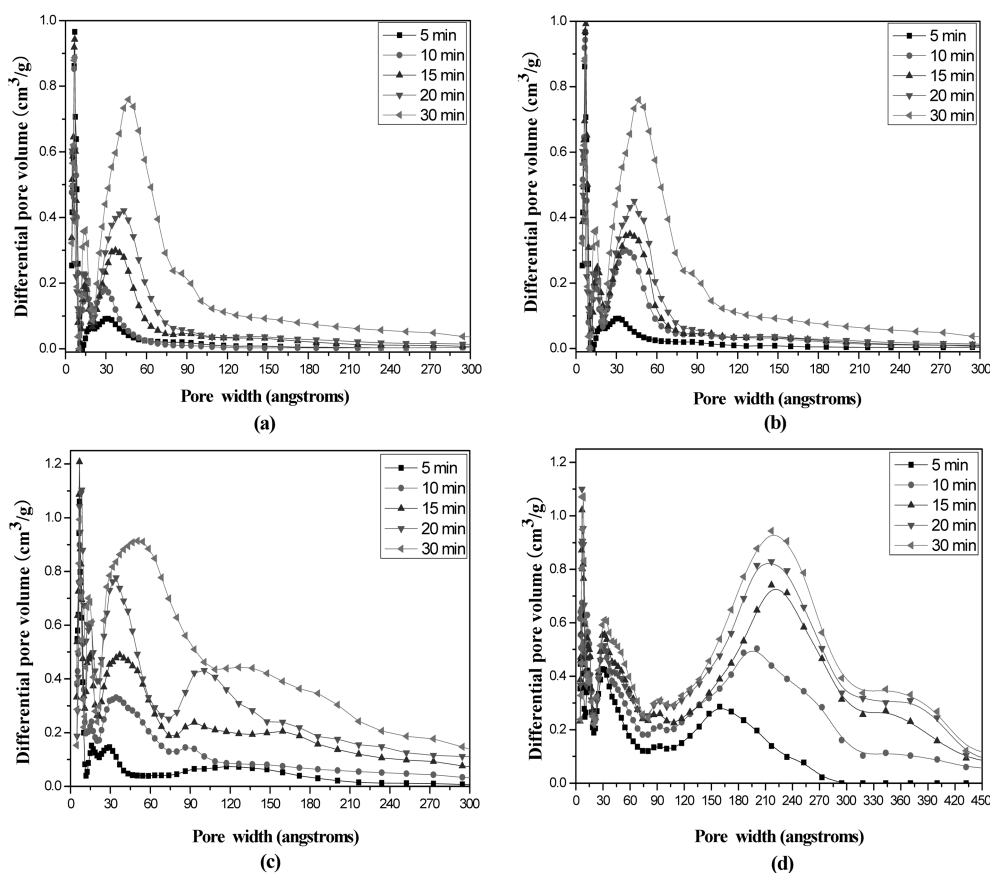


Fig. 8. Pore size distributions of AHFs activated at different time and temp : (a) 600, (b) 700, (c) 800, and (d) 900°C.

at 77 K. The isotherms of AHF prepared at 600°C show type I indicating the development of micropores. However, the isotherms prepared over 700°C show hysteresis loops which indicates the Type IV isotherm and lots of micropores were changed to mesopores by increasing the activation temperature. Also, the increased adsorption amount indicates the increase of total pore volume by increasing the activation temperature over 700°C.

Fig. 8 shows the pore size distributions of AHF with different activation times and temperatures. The respective pore volumes calculated on the basis of nitrogen isotherm in (a), (b), (c), and (d) in Table 3 were compared each other. From the figures, the pore size distribution was distinctly moved to larger pore width as increasing the activation temperature and bimodal distribution was appeared above 800°C. Also, it appears that the difference in the heating rate during carbonization has influenced the formation of micro- and mesopores significantly during subsequent steam activation. The increased heating rate during carbonization leads to the increase mesopore volume in the AHF.

3.4. Methylene blue decolorization of AHF

Fig. 9 shows methylene blue decolorization capacity of

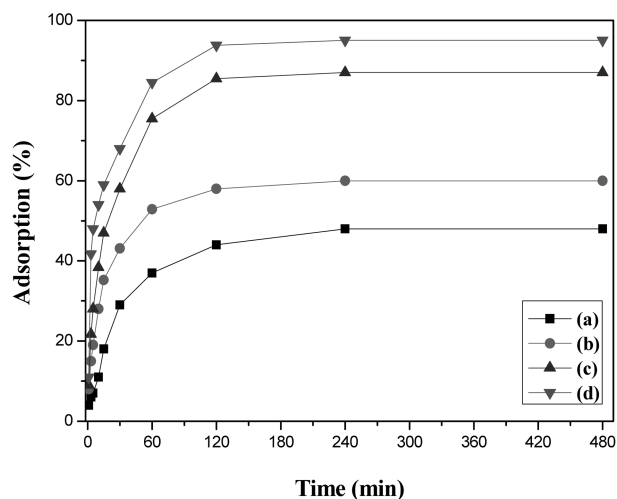


Fig. 9. Methylene blue decolorization capacity of AHF prepared at (a) 600, (b) 700, (c) 800, and (d) 900°C for 30 min (MB Conc.: 600 ppm, 0.1 g AHF in 100 ml aqueous solution).

AHF prepared at 600, 700, 800, and 900°C for 30 min. without agitation. The decolorization of methylene blue was rapidly increased, especially in the beginning stage on AHF and the capacity of was proportional to the increase of

activated temperature, which means the increase of specific surface area or total pore volume. In this experiment, the AHF prepared at 900°C for 30 min adsorbed the methylene blue about 570 mg/g-AHF for 2 hr. In view of the adsorption rate and amount of fibrous adsorbents were rapidly enhanced by agitation, the decolorization capacity of AHF can be enhanced by agitation. With these results, promisable natural cellulose based fibrous adsorbent, AHF, can be obtained by proper stabilization, carbonization, and steam activation.

4. Conclusions

Natural cellulose based fibrous adsorbents having more than 1300 m²/g specific surface area and 1.1 cm³/g pore volume can be prepared from henequen by stabilization, carbonization, and steam activation. The optimum conditions of each stage can be selected in consideration of yield. Structural characteristics were significantly influenced by the activation temperature and time. Only micropores developed AHF can be obtained from carbonized henequen fiber within 10 min. activation time between 600~1000°C, however as increasing the activation time over 10 min, lots of micropores developed were changed to mesopores showing a bimodal pore size distribution. The prepared AHF shows good methylene blue decolorization capacity.

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