Synthesis of Activated Carbon from Rice Husk Using Microwave Heating Induced KOH Activation

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Abstract The production of functional activated carbon materials starting from inexpensive natural precursors using environmentally friendly and economically effective processes has attracted much attention in the areas of material science and technology. In particular, the use of plant biomass to produce functional carbonaceous materials has attracted a great deal of attention in various aspects. In this study the preparation of activated carbon has been attempted from rice husks via a chemical activation-assisted microwave system. The rice husks were milled via attrition milling with aluminum balls, and then carbonized under purified N₂. The operational parameters including the activation agents, chemical impregnation weight ratio of the calcined rice husk to KOH (1:1, 1:2 and 1:4), microwave power heating within irradiation time (3-5 min), and the second activation process on the adsorption capability were investigated. Experimental results were investigated using XRD, FT-IR, and SEM. It was found that the BET surface area of activated carbons irrespective of the activation agent resulted in surface area. The activated carbons prepared by microwave heating with an activation process have higher surface area and larger average pore size than those prepared by activation without microwave heating when the ratio with KOH solution was the same. The activation time using microwave heating and the chemical impregnation ratio with KOH solution were varied to determine the optimal method for obtaining high surface area activated carbon (1505 m²/g).

Key words activated carbon, rice husk, microwave, KOH, BET.

1. Introduction

Recently, activated carbon has known as its large porous surface area and controllable pore structure. Activated carbons are carbonaceous materials and the materials starting from cheap natural precursors that can be produced by physical and chemical activation. The significant things are the high surface area and complex pore structure resulting from physical or chemical activation processes. The commonly used precursors to prepared activated carbon are bituminous coal,¹⁻³⁾ wood,⁴⁻⁶⁾ coconut shell,⁷⁻⁹⁾ polymers,^{10,11)} and so on. However, rice husk is one of the most popular material with low cost. In some reports, activated carbons were prepared from rice husks by chemical activation with KOH, NaOH, Na₂CO₃, ZnCl₂, and so on, at different temperatures for various times.^{12,13)} The previous researches have demonstrated the ability of rice husk-based activated carbon for many metal ions and organic molecules from aqueous phase adsorption.

Activated carbon, by its wonderful structure, has been applied in various industries for several years: it is used for the separation of gases, recovery of solvent and re-

moval of organic pollution.¹⁴⁾ The applications of activated carbons are also expanded, such as super-capacitors, electrodes and gas storage,¹⁵⁻¹⁷⁾ which require the activated carbons containing a higher surface area. The activated carbon structure properties have been demonstrated to be effective for removal of a wide variety of inorganic¹⁸⁻²⁰⁾ and organic^{21,22)} pollutants dissolved in aqueous media, or from gaseous environment.²³⁾

Activated carbons have been prepared by many synthesis methods such as carbonization process, chemical agent activation, microwave heating. The use of alkali hydroxides such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) as activating agents for the production of microporous activated carbon had attracted great interest due to the valuable properties of the materials produced by this process. For preparation of activated carbons, conventional heating method is usually adopted. Recently, microwave heating technology has been applied to fabricate activated carbons due to its heating rapidly and uniformly. The main reason for the use of microwave is that microwave power is a predominant factor affecting the adsorption uptake capacity and carbon yield. Enhancing microwave power led to increase of adsorption uptake, possibly ascribed to the combined effect of internal and volumetric heating responsible for the expansion of carbon

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structure.

Actually, as far as we know, there are few reports on the preparation of activated carbon by a combined chemical activation and microwave heating.²⁴⁾ The primary objective of this study was to produce activated carbon adsorbents from rice husk by KOH as chemical activation and microwave heating, and then attempt the effect of the high surface area activated carbon prepared by a combined chemical activation and microwave heating.

2. Experimental Procedure

In this study, the rice husks (RH) was supplied by the Hyunduk industry production (Korea) as raw materials. They were washed with DI water in the ultrasonic cleaner to remove dirt and other contaminants present in them and then dried in the dry oven at about 60-70°C for 24 hours. Then, the dried RH was milled by the attrition milling with alumina balls ($\varnothing$ 2 mm). Settings for the attrition milling operate 600 rpm for 1 hour. The milled samples were sieved through different size sieves. In this work, the particle size of less than 425 μ m was selected for further pretreatment. After that, the experiment was carried out carbonization for the samples. In particular, the sieved samples were tipped into an alumina boat and then put inside the tube furnace. In order to perform carbonization process, heat treatment was carried out under purified N₂ with a flow ratio of 300 ml/min for 2 hours at 700-800°C. The black calcined RH was obtained by carbonization process.

The next step was chemical activation for black calcined RH. In the present work, KOH was chosen as the chemical activating agent. KOH solution is very effective to remove in the organics and they dissolve the silica which contains in the RH. Based on the main objective to get the activated carbon, the black calcined RH was carried out soaking treatment in KOH solution. In chemical impregnation, the weight ratio of black calcined RH to KOH was corresponding to 1:1, 1:2 and 1:4. For example, in case of ratio of black calcined RH : KOH is 1:2, 1 gram of black calcined RH was dispersed and soaked in KOH solution with 2 gram KOH in 100 ml DI water. The RH soaked in KOH solution were stirred and dried until paste state by the hot plate at 60°C and then the paste samples were dried in the dry oven at 60°C for several hours.

The dried paste was carried out heating by microwave irradiation (90-800 W) for 3-5 minutes. The samples were washed in ultrasonics machine and then dried for several hours before preparing activation in the tube furnace again. The second activation was performed at different temperature in the range of 700 to 900°C for 3 hours. The final step was washing the samples in 100 ml DI water at 100°C, and filtering. The activated carbon (AC) have got

Fig. 1. Schematic representation of processing steps for the synthesis of activated carbon derived from rice husk.

after drying of the filtered char. All of the processing steps for the synthesis of activated carbon derived from rice husk were clearly exhibited in the schematic in Fig. 1.

The activated carbon was characterized to determine crystal structure by measurement of X-ray diffraction (XRD, CuK α radiation (λ = 0.15418 nm), D1w, Shimadzu, Japan) over the 2θ range from 20° to 80° at a scan rate of 2°/min. Besides, particle size and morphology were observed by scanning electron microscope for observation SEM (Sirion, FEI, Netherland). Fourier-transform infrared (FT-IR) spectra were recorded with a FT-IR Frontier from PerkinElmer. The transmittance of pellets consisted of 10 mg of the powder sample and 1 g KBr, and was measured in a wavenumber interval of 800-2000 cm⁻¹. Specific surface area determinations were performed by

Table 1. Experimental parameters and porous structure parameters of activated carbon derived from rice husk in activation condition at 700°C for 3h.

Sample	Carbonization Temp. (°C)	Char : KOH	Microwave heating (min)	Activation Temp. (°C)	Average Pore size (Å)	Micropore Volume (cm ³ /g)
AC7117	700	1:1	0	700	29.6	0.35
AC7117-3			3		27.4	0.34
AC7127	700	1:2	0	700	22.0	0.41
AC7127-3			3		30.9	0.37
AC7147	700	1:4	0	700	22.6	0.58
AC7147-3			3		63.4	0.49

Table 2. Experimental parameters and porous structure parameters of activated carbon derived from rice husk in various activation conditions at 800°C and 900°C for 3h.

Sample	Carbonization Temp. (°C)	Char : KOH	Microwave heating (min)	Activation Temp. (°C)	Average Pore size (Å)	Micropore Volume (cm ³ /g)
AC7118	700	1:1	0	800	25.2	0.43
AC7118-3			3		28.5	0.32
AC7128	700	1:2	0	800	21.4	0.72
AC7128-3			3	800	22.3	0.42
AC7129-3			3	900	29.4	0.39
AC7148	700	1:4	0	800	23.3	0.77
AC7148-3			3		25.7	0.34
AC7148-5			5		19.9	0.55

the surface areas, average pore size and micropore volumes of the activated carbons using the Brunauer-Emmett-Teller (BET) method with an adsorption meter of N₂ (model ASAP 2010 micromeritics).

3. Results and Discussion

One thing to admit that specific surface area parameter (BET) is an important factor to estimate porous character and micropore structure. Thus, in this study, various experimental parameters were prepared and labeled as described in Table 1 and Table 2. Table 1 and Table 2 gives information on porous structure parameters of activated carbon derived from RH in various conditions. It is clearly realized effective factors on the specific surface area (S_{BET}) such as weight ratio of char:KOH, microwave heating process and activation temperatures.

3.1 Characteristic of activated carbon

The structural parameters and features of the activated carbons were obtained from the XRD analysis. The XRD results from activated carbons synthesized by activating at 700°C for 3h using a combined soaking in various KOH weight ratio and microwave heating for 3 minutes are shown in Fig. 2. The XRD pattern of activated carbon basically appears the non-crystalline form. In the vicinity of $2\theta \approx 25-26^\circ$, the XRD pattern was shown wide width

Fig. 2. XRD patterns of activated carbon synthesized by activating at 700°C for 3 hours using a combined soaking in various KOH weight ratio and microwave heating for 3 minutes: (a) 1:1 (AC7117-3), (b) 1:2 (AC7127-3) and (c) 1:4 (AC7147-3).

and asymmetric peak. The XRD pattern of $2\theta \approx 26^\circ$, corresponding to (002) peak, was observed to appear with increasing concentration of KOH solution. Interestingly, only the diffraction peaks typical of activated carbon were seen in the XRD pattern and no indication of impurities is observed. This indicates the effectiveness and also the significance of the treatment with a base solution. Phase

Fig. 3. SEM photographs of activated carbon synthesized by activating at 700°C for 3 hours using a combined soaking in various KOH weight ratio and microwave heating for 3-5 minutes: (a) AC7117-3, (b) AC7127-3, (c) AC7147-3 and (d) AC7148-5.

structure of activated carbon was affected by ratio of char : KOH.

Scanning electron microscopy (SEM) micrographs of activated carbon synthesized by activating at 700°C for 3 hours using a combined soaking in various KOH weight ratio and microwave heating for 3-5 minutes are given in Fig. 3. Based on the SEM images, the structure of activated carbon was porous with many pores. Although applying the microwave system with longer irradiation time (5 minutes) as shown in Fig. 3(d) sample, the activated carbon structure was not more porous as the samples structure which was activated for 3 minutes microwave. This result was shown clearly in Fig. 3(d) and the above Table 1. With increasing concentration of KOH solution, average pore size increases. However, in Fig. 3(d) sample obtained by longer irradiation time of microwave, average pore size decreases.

Fig. 4 shows XRD patterns of activated carbon nanopowders synthesized by activating at 800°C for 3h using a combined soaking in various KOH weight ratio and microwave heating for 3 minutes. The only different point is intensity of peak as the effect of activation temperature on the structure of activated carbon. When the weight ratio of char : KOH is 1:1, the intensity of peak of activated carbons increase with increasing activation temperature. The two broad peaks are observed at 26° and 44° typical of activated carbons, corresponding to (002) and (101) in the XRD pattern, respectively (JCPDS 12-

Fig. 4. XRD patterns of activated carbon synthesized by activating at 800°C for 3 hours using a combined soaking in various KOH weight ratio and microwave heating for 3 minutes: (a) 1:1 (AC7118-3), (b) 1:2 (AC7128-3) and (c) 1:4 (AC7148-3).

0212). Especially, partly crystallization was observed in the sample soaking ratio of 1:1 KOH solution combining activation at 800°C (AC7118-3) as shown in the Fig. 4. However, no main peak is observed for the samples with increasing concentration of KOH solution probably due to an effect on the structure of activated carbon by a variation of the internal structure.

Fig. 5 shows the SEM photographs of activated carbon synthesized by activating at 800°C for 3 hours using a

Fig. 5. SEM photographs of activated carbon synthesized by activating at 800°C for 3 hours using a combined soaking in various KOH weight ratio and microwave heating for 3-5 minutes: (a) AC7118-3, (b) AC7128-3, (c) AC7148-3 and (d) AC7129-3.

combined soaking in various KOH weight ratio and microwave heating for 3 minutes. With increasing concentration of KOH solution, average pore size decreases. Also, the activated carbons treated at the higher activa-

tion temperature tend to be dense compare with the sample of Fig. 3.

The surface of carbon materials is, in general, rich in a variety of surface functional groups among which the C-O type groups are predominant. To know the specific type of functional groups present on the surface, the activated carbon materials were analyzed by FT-IR analysis.

The FT-IR spectra of the activated carbon synthesized by activating from 700°C and 800°C for 3 hours using a combined soaking in various KOH weight ratio and microwave heating for 3 minutes were shown in Fig. 6. It can be noticed that for all the carbons the peaks at 1212.08 cm^{-1} is observed and their reason is the CO group (stretch of C=O). In addition, the creation of bands at 1489.01, 1497.29, 1566.17 and 1559.65 cm^{-1} can be results of the ionic form of carboxylic groups.²⁵⁾

Fig. 6. FTIR spectra of activated carbon synthesized by various activating temperature for 3 hours using a combined soaking in various KOH weight ratio and microwave heating for 3 minutes: (a) AC7127-3, (b) AC7147-3, (c) AC7128-3 and (d) AC7148-3.

3.2. Effect of activation temperatures and microwave heating process

The second activation process was carried out at range of 700 to 900°C for 3 hours under purified N_2 gas. According to the afore-mentioned Table 1, it is clearly seen that porous properties of activated carbons changed with the change of activation temperatures.

Fig. 7 shows the effect of activation temperatures on specific surface area BET (S_{BET}) parameters of the activated carbon samples. As can be seen, the specific surface areas of the activated carbons at 800°C had higher than

Fig. 7. Diagram representation of effect of activation temperatures (700 and 800°C) on BET surface areas of activated carbon.

Fig. 8. Diagram representation of effect of microwave heating process on surface areas BET of activated carbon activating at 700 and 800°C.

those of the activated carbons at 700°C. However, in case of activation at 700°C, the samples tended to increase S_{BET} according to rate of char : KOH. This result is one of the evidences that express the influence of concentration of KOH solution on S_{BET} of activated carbon. In the activated carbons at 800°C, the highest S_{BET} for sample that soaked with KOH according to ratio of 1:2 was 1505 m^2/g . However, the S_{BET} decreased to 1254 m^2/g corresponding to ratio of 1:4 (char : KOH). In general, at higher activation temperature, specific surface area of activated carbon tends to increase significantly.

The present work also attempted synthesis activated carbon without microwave. These samples have surface areas that were shown on the Table 1 and Table 2 without microwave heating.

Based on the above diagram in Fig. 8, it is clearly seen that the use of microwave to heat the samples before

carrying out the second activation affected surface area of activated carbon. In particular, the synthesis of activated carbon using microwave heating before activation 700°C according to the ratio of corresponding char : KOH got the positive results making the samples that have S_{BET} higher than the synthesized samples without microwave. Especially, the sample AC7117-3 (microwave 3 minutes) has S_{BET} (775 m^2/g) was double than the sample AC7113 (without microwave) with the lowest surface area value (482 m^2/g). At 700°C activation, S_{BET} value of activated carbon went up corresponding to rate of precursor samples with KOH (1:1, 1:2 and 1:4). This result, one more time, apparently indicated the effect of rate of soaking char with KOH on S_{BET} of activated carbon.

Likewise, Fig. 8 showed the diagram that illustrated the effect of microwave heating process on BET surface areas of activated carbon activating at 800°C. BET surface area of these samples tended to increase from condition soaking ratio of 1:1 with KOH and reached peak of the highest S_{BET} at condition 1:2 before decreasing at condition 1:4. However, the sample that was heated by microwave in condition 1:2 having the highest S_{BET} . In addition, Table 1 also indicated that the microwave heating affected pore size of active carbon. If we estimate and compare in the same of soaking KOH : char condition, the average pore size of the samples that were synthesized using microwave treatment were more bigger than that of other synthesized samples without microwave. One thing to note that the sample AC7147-3 (rate with KOH 1:4, activation temperature 700°C, 3 minutes microwave treatment) has the maximum average pore size just over 63 Å.

4. Conclusion

In this study, the activated carbon were synthesized by chemical activation method and microwave heating with various activating temperatures and ratio of char : KOH, the phase structure of activated carbon was investigated and observed. The XRD pattern of activated carbon basically appears the non-crystalline form at the activation temperature 700°C, however, partly crystallization was observed in the sample soaking ratio of 1:1 KOH solution combining activation at 800°C.

In summary, microwave heating method can provide an efficient way to prepare activated carbons with high surface area. It is interesting to admit that the activated carbons prepared by microwave heating method present higher S_{BET} compared to those prepared by method without microwave when KOH/char ratio is the same.

The S_{BET} increases with the increase in KOH/char ratio in the range of 1:1 and 1:2, and then decreases with the further increase in the ratio for each heating method at rate of 1:4 in the case of activation 800°C. When activation

process was carried out at 700°C, surface areas tend to rise significantly corresponding to increase in the ratio of char : KOH. There is relation between activation temperature, ratio of soaking char and KOH solution and microwave heating. The research would attempt more the effect of microwave time as well as activation temperature in the future. The change of surface and internal structure were exhibited clearly by the above evidence.

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