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Investigation on physical activation of some Mongolian coals

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ABSTRACT

Activation characteristics of four different Mongolian coals were investigated. The coals were carbonized at temperatures of 550 °C and the obtained samples were activated by preheated steam. The pore size, pore volume and surface areas of all activated carbons (AC) have been determined by adsorption of nitrogen (N_2) gas. The BET surface areas of Aduunchuluun (ACAC), Shivee Ovoo (SCAC), Baganuur (BCAC) coal and Ulaan Ovoo coals (UCAC) are 283, 205, 251 and 460 m^2/g respectively. Langmuir surface area is 283 m^2/g of ACAC, 230 m^2/g of SCAC, 537 m^2/g in UCAC and 254 m^2/g in BCAC.

Keywords: Carbonization, activation, surface area, micropores, mesopores

INTRODUCTION

Coals of varying quality are considered to be an abundant source for the manufacturing of activated carbons (AC). The activated carbons are often used as the adsorbents for removing impurities from drinking water, industrial outlet gases. Furthermore, ACs are basic materials of catalysts in the chemical industry, different kinds of coals are more frequently used as carbon resources for ACs. ACs are used as filtering and adsorbent materials for cleaning of toxic gas, drinking water, industrial wastewater and so on. Furthermore, ACs are bases of catalyst in the chemical industry, medicines in healthcare and special absorbent for cleaning the human blood [1]. Indeed, many conventional methods have been used for wastewater treatment such as precipitation, oxidation, flotation-coagulation, and electrocoagulation. Even they appear effective, they are limited to a variety of pollutant for technical reasons and a high cost of exploitation or may not be capable of treating large volumes of effluent [2]. Among the above mentioned methods for wastewater treatments that has drawn attention to many researchers in the last decades, adsorption using AC, a phase transfer process has been widely used in practice to remove contaminants in all their forms (organic and inorganic) from fluid phases because of the low investment in initial cost and design simplicity [3]. Therefore, the study of ACs characteristics obtained from coal is of viable importance nowadays. We have investigated above mentioned 4 coals from different deposits in Mongolia by physical activation method. Before activation, each coal sample was carbonized by pyrolysis at 550-650 °C for 120 min for the porous characteristics such as BET and Langmuir surface area, pore volume and pore size in ACs obtained from the coals.

EXPERIMENTAL

The ultimate and proximate analyses of coals used for the present study are shown in Table 1. The coals were pulverized, ground and sieved, and the samples with particle sizes between 1.5 - 3 mm were selected the carbonization experiment. Approximately 400 grams of samples were loaded into the SNOL reactor and closed tightly to prevent any leakage. The reactor was switched on and the temperature was increased with the heating rate of 20 °C/min up to 550 - 600 °C. At this final temperature, the carbonization was continued for 120 minutes. The volatile products released during the carbonization process cooled down and liquid products

were separated from the gaseous components by condensation. The yields of gaseous, liquid and solid products were determined by the weight difference. The solid residue called as a semi-coke obtained from the thermal decomposition of coal has been used as a sample for the preparation of activated carbon.

The semi-coke was sieved and the fractions with the particle size of 0.63 - 1.5 mm have been selected as an experimental sample. The 15 grams of the samples were loaded into a horizontal reactor and closed without any leakage. Afterward, the temperature was raised up to 800 °C with a heating rate of 5 °C/min. When the temperature inside the reactor was stabilized the saturated steam with the flow rate of 160 cm^3/min was introduced into the reactor for 90 minutes.

The methodology for the determination of surface area, pore volume, pore size: The surface area of the activated carbon was determined by the adsorption of nitrogen with the flow rate of 3 cm^3/min at STP. The surface area of the sample (Sg_x) is calculated using the following equation:

$$Sg_x = \frac{A_x \times W_o}{A_o \times W_x} \times Sg_o$$

Where, A_o and A_x are desorption area of the standard sample and the experimental sample, W_o and W_x sample and represent the weight of standard sample and experimental sample, Sg_0 is surface area of the standard sample [4, 5].

The method of determining porous structure of AC by SEM analysis: The porous structure of ACs was observed by SEM. The SEM is made in Nikkiso Company of Japan, SEMTRAC mini SM-3000 mark, in high vacuum condition, with second electron detector, raiser up to 20-30.00 V, and voltage 20 kV. Prepared samples were covered by gold metal after putting in the sample plat. The covered time is 60 sec and the gold tin is 5-10 nm [6].

RESULTS AND DISCUSSION

The results of the proximate and ultimate analysis of initial coal samples from Shivee Ovoo, Ulaan Ovoo, Aduunchuluun, and Baganuur deposits are shown in Table 1. The brown coal is considered to be a relatively cheap raw material for preparation of AC. Nevertheless, some studies indicated that some coals contain more ash and sulfur and are not suitable for activation. For our selected coals, the ash content of Shivee Ovoo coal is higher (21.17 %) compared to the other three coals (Table 1). According to the proximate and ultimate analysis, the coals we studied showed close results to each other. The sample was pyrolyzed to the temperature of 550 - 600 °C with a heating rate of 20 °C/min for 120 minutes and the result shown in Table 2. Table 2 shows the solid residues (semi-coke) yield of pyrolysis 52-59 % and the yields of thermal decompositions were generally approximate because the coals were with similar properties (Table1).

Table 1. The results of proximate and ultimate analyses of coals

Deposit location	Shivee Ovoo	Ulaan Ovoo	Baganuur	Aduunchuluun
Coal type	Lignite	Subbituminous coal	Lignite	Lignite
Proximate analysis, %				
Moisture, W^a	13.41	5.10	9.40	20.16
Volatile matter, V^{daf*}	42.57	46.8	47.0	48.0
Ash, A^d	21.17	4.90	13.30	13.50
Caloric value, Q^{daf}, kcal/kg	6501	6218	5257	6363
Ultimate analysis, %				
Carbon, C^{daf}	71.36	74.6	70.5	66.75
Hydrogen, H^{daf}	4.99	4.6	5.7	4.93
Nitrogen and oxygen, $(N+O)^{daf}$	22.59	31.40	41.50	26.10
Sulfur, St	1.06	0.54	0.51	2.22

**daf - dry ash free*

Table 2. The yields of pyrolysis products at 550- 650°C

Samples	Solid residues, %	Liquid products, %	Gas and loss, %
Shivee Ovoo	59.0	22.4	18.6
Aduunchuluun	52.3	25.2	22.4
Baganuur	59.3	36.5	4.15
Ulaan Ovoo	58.3	22.2	19.5

Table 3. Main technical characteristics of the pyrolysis solid residue of coals

Samples	Moisture,% W^a	Ash, % A^d	Volatile matters, % V^{daf}	Caloric value, Q^{daf}, Kcal/Kg
Shivee Ovoo	0.1	27.4	16.2	7337.9
Aduunchuluun	0.1	21.0	8.1	7126.3
Baganuur	2.8	13.9	8.3	6802.0
Ulaan Ovoo	0.8	24.7	4.3	6910.0

Table 4. The result of activation by preheated water steam, and yield of AC, methylene blue and iodine absorption

Samples	T, °C	Time min	Yield %	Absorption, mg/g	
				Iodine	Methylene blue
Shivee Ovoo	800	90	51.6	26.3	373.8
Aduunchuluun	800	90	54.3	28.1	366.3
Baganuur	800	90	50.3	25.8	372.5
Ulaan Ovoo	800	90	82.5	48.5	247.4

During carbonization, was formed a semi-coke that is one of the main products and used to prepare AC after activation. For this reason, we have determined the main technical characteristics of the solid residue in (Table 3). In Table 3, the volatile matter content decreased 10 times for Ulaan Ovoo coal and it might form a more porous structure than others. For this reason, the semi coke produced after pyrolysis was activated by preheated water steam at 800 °C for 90 min. Before activation, semi-coke was sieved 0.63 mm pieces. The result of determined yield of AC, methylene blue, and iodine absorption are shown in Table 4. The iodine absorption presents micropores of AC and methylene blue absorption presents the size of mesopores. As shown in Table 4, the yield of activated coals is 50.3 - 51.6 % in brown coals (Aduunchuluun, Shivee Ovoo, Baganuur) and 82.5 % in sub-bituminous coal (Ulaan Ovoo). The iodine absorption had more (48.5 %) in AC of Ulaan Ovoo coal than other ACs. In general, the iodine absorption has 500 - 1200 mg/g in commercial AC [6]. From this point of view, our AC has less microporous than commercial AC. The surface area pore volume, pore size of the activated carbon was determined by the adsorption nitrogen. The isotherm linear of four ACs has been shown in Figure1. This isotherm linear indicates how the volume of the nitrogen absorbed at constant temperature and relative pressure.

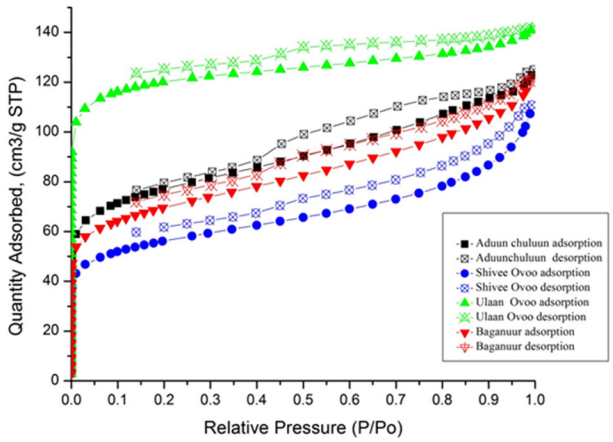

Fig. 1. Isotherm linear plot of ACs

From Figure 1, it can be obtained that the curve is complex and a combination of several physisorption isotherms types. In the part of low relative pressure, there is a large adsorption capacity, which is close to the adsorption isotherm of type I, and close to type II with the relative pressure increases, but the hysteresis Loops is type H4 according to the IUPAC classification, and type H4 loops are also often associated with narrow slit pores, type H4 are often found with micro-mesoporous carbons [4].

The AC of Ulaan Ovoo coal (maximum 130-140 cm^3/g) had more nitrogen absorption than others, and other deposits of activated carbons nitrogen absorption are approximate 100-120 cm^3/g. The estimate of activated carbon surface area is based on the BET method using nitrogen physical adsorption.

The Brunauer-Emmett-Teller method continues to be the most widely used procedure for evaluating the surface area of porous and finely-divided materials, in spite of the weakness of its theoretical foundations. Indeed, under certain carefully controlled conditions, the BET-area of a nonporous, macroporous or a mesoporous solid (i.e., giving a well-defined type II or a type IV(a) isotherm) can be regarded as the 'probe accessible area' (i.e., the effective area available for the adsorption of the specified adsorptive). According to the BET theory related to the multilayer adsorption, and Langmuir surface area related to the monolayer adsorption [7]. The results of determining the surface area of BET and Langmuir in the activated coals are shown in Table 5.

Table 5. BET and Langmuir surface area of AC

Samples	ACAC	SCAC	UCAC	BCAC
Langmuir surface area, m^2/g	283	205	460	251
BET surface area, m^2/g	283	230	537	254

As shown in results, the BET surface area is 283 m^2/g in ACAC, 205 m^2/g in SCAC, 460 m^2/g in UCAC and 251 m^2/g in BCAC. And Langmuir surface area is 283 m^2/g in ACAC, 230 m^2/g in SCAC, 537 m^2/g in UCAC and 254 m^2/g BCAC. Generally, the BET surface area of trading activated carbon is 10-400 m^2/g in the surface of mesoporous, whereas the micropores are 500-2000 m^2/g, while the surface area of our UCAC is near the standard of micropores while others are very small mesoporous predominates. One of the methods determining the pore size and pore volume is BJH analysis. BJH analysis can also be employed to determine pore area, average pore width (4 V/A) and specific pore volume using adsorption and desorption techniques. This technique characterizes pore size distribution independent of the external area due to the particle size of the sample [6, 7]. The result of BJH adsorption cumulative pore volume and BJH desorption

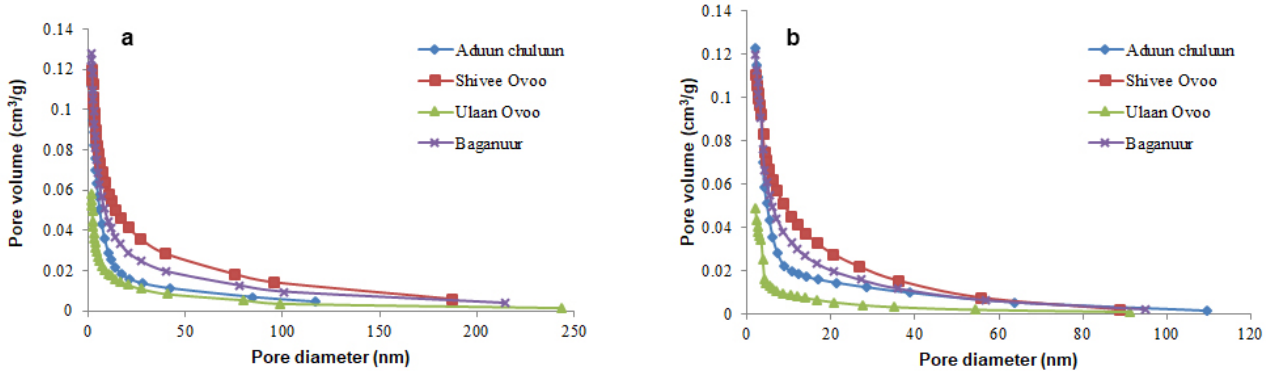

Fig. 2. The distribution curve of porous for activated carbons, a - adsoption; b - desorption

cumulative pore volume are presented in Figure 2.

BJH pore size distribution graph and data adsorption of ACs cumulative volume of pores between 1.7 and 300 nm diameter in BCAC 0.13 cm^3/g, ACAC 0.12 cm^3/g, SCAC 0.12 cm^3/g and UCAC 0.06 cm^3/g, and BJH desorption of ACs cumulative volume of pores between 1.7 and 300 nm diameter in BCAC 0.12 cm^3/g, ACAC 0.12 cm^3/g, SCAC 0.11 cm^3/g and UCAC 0.06 cm^3/g. The BJH adsorption pore volume is not greater than 0.7 cm^3/g. In addition, the pore volume and pore distribution of activated carbons are determined by the Horvath-Kawazoe method [5] and the result is shown in Table 6. As shown in Table 6, the adsorption average pore width (by the BET method) in SCAC 3.33 nm, BCAC is 2.97 nm, ACAC is 2.72 nm, and UCAC is 1.9 nm. And the median pore width of SCAC is 0.48 nm, BCAC is 0.48 nm, ACAC is 0.47 nm, and UCAC is 0.46 nm and there is more pore distribution with 0.4-0.6 nm.

The images of scanning electron microscopes (SEM) of activation carbons presented in Figure 3.

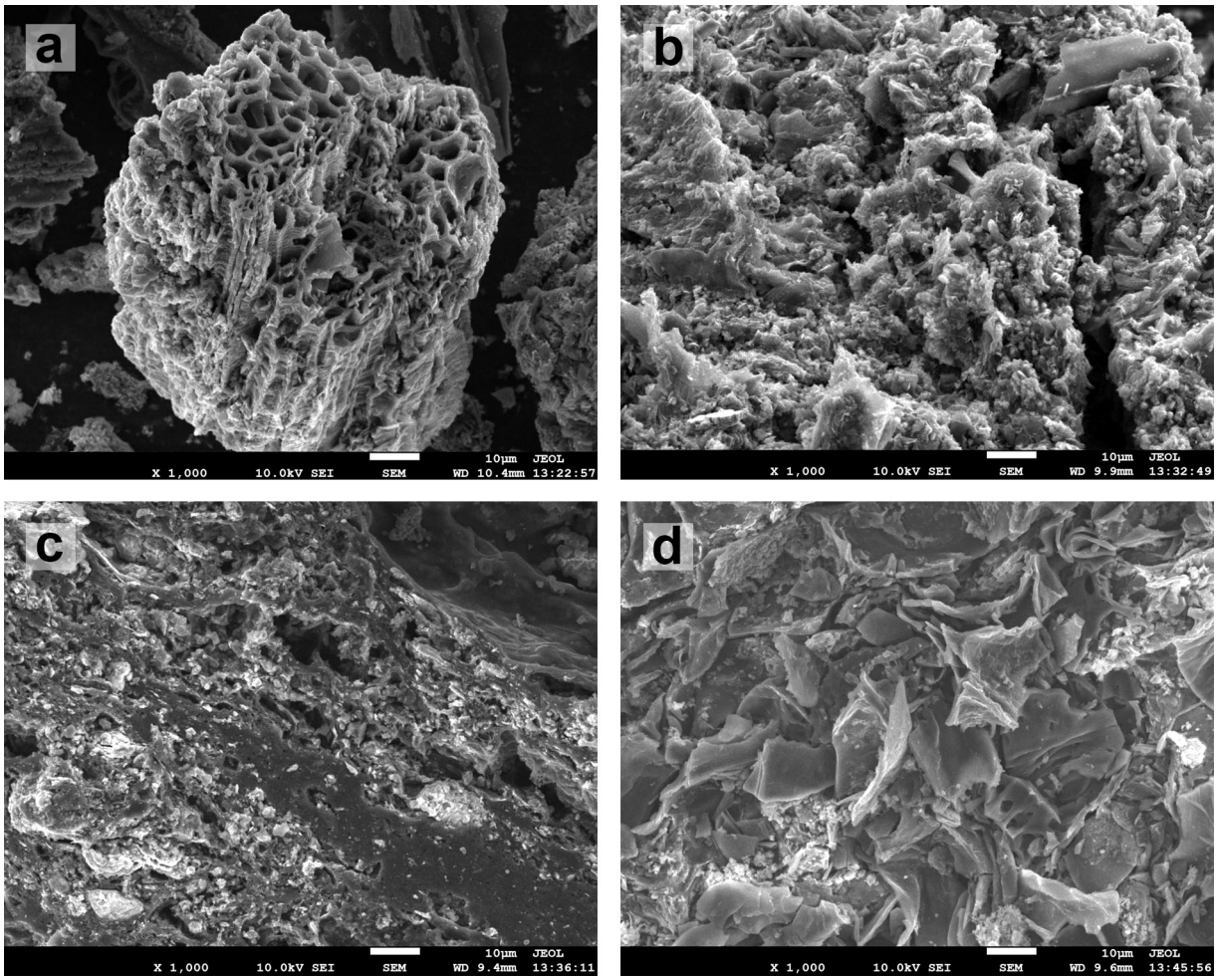

Fig. 3. SEM analysis of ACs, a - Aduunchuluun, b - Shivee Ovoo, c - Ulaan Ovoo, d - Baganuur

Table 6. Horvath-Kawazoe cumulative volume and differential pore volume of AC

Samples	Pore width, nm	Median pore width, nm
SCAC	3.33	0.48
BCAC	2.97	0.48
ACAC	2.72	0.47
UCAC	1.90	0.46

The SEM analysis shows that pore structure is different for each coal and it can be observed in different sizes and shape pores. For example, in Figures 3b, 3c, and 3d, the pore distribution is uneven and the hardness of the pores is not noticeable, which may indicate that the activation may be incomplete. The incomplete activation depends on coal characterization and processing to activation and which negatively affects the pore structure and the surface area. Figure 3a has relatively large fluffy fibrous and there are macropores that are more obvious.

CONCLUSION

The activated carbon of Ulaan Ovoo coal had more nitrogen adsorption than others. In the case of Ulaan Ovoo coal of iodine absorption, BET surface area, and Langmuir surface area are close to the standard for the micro-surface area of activated carbon and the other coals have very fewer micropores.

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