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Preparation and characterization of activated carbons from different kinds of coal

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Abstract: Initial coal was purified in heavy liquid with a density 1.3 cm^3 of ZnCl_2 solution and purified coal was carbonized and the initial coal samples of each deposits were purified by pyrolysis. Thus, the yield of pyrolysis hard residue in the enriched sample was slightly higher than in the hard residue of initial coal. Therefore, pyrolysis hard residue of purified coal (carbonized sample) was activated at 800°C for 2 hours by preheated water steam. Activated carbons (ACs) and non-activated and non-carbonized coal from Baganuur, Ereen and Nariin Sukhait deposits were technically analyzed and their iodine number, BET surface area, pore volume and adsorption of methylene blue (MB) were determined. When these results were compared, these indicators increased 5-17 times in the Baganuur activated carbon (BN-AC), Ereen activated carbon (E-AC) and Nariin Sukhait activated carbon (NS-AC) as compared to inactivated coal.

Keywords: adsorption; methylene blue; activated carbon; Iodine number; surface area;

INTRODUCTION

The consumption of activated carbon is continuously growing in as much as they are used in such important areas as waste and potable water treatment, atmospheric pollution control, poisonous gas separation, solvent recovery, etc. Almost any carbonaceous material can be converted into activated carbon [1-2]. In general, activated carbons with both a high surface area and porosity, allowing large amounts of adsorption, are desirable. The pore

structure is the most important property of activated carbon. It was earlier believed that the carbon had to be activated by chemical and heat treatment before it could remove color, hence the name activated carbon.

Activated carbons can be prepared in the laboratory from a large number of materials, but the most commonly used materials in commercial practice are peat, coal, lignite, wood and coconut shell [3].

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Small diameter pores with internal surface areas in the range 500-1500 m² per gram are found in residues from carbonization and activation, and it is this enormous area that makes them effective adsorbents [4]. The principal properties of manufactured active carbons depend on the type and properties of the raw material used. The basic method of activating coal-based granules consists of their treatment with oxidizing gases (steam, carbon dioxide, oxygen) at elevated temperatures. In the activation process, carbon reacts with the oxidizing agent and the resulting carbon oxides diffuse from the carbon surface [5]. Owing to the partial gasification of the granules or grains, a porous structure builds inside them. Another important activation process is chemical activation, where non-carbonized raw materials such as peat and sawdust are used [6]. Indeed, many conventional methods have been used for wastewater treatment such as precipitation, oxidation, flotation-coagulation, and electrocoagulation. Although they appear

effective, they are limited to a variety of pollutants for technical reasons and a high cost of exploitation, or may not at all be capable of treating large volumes of effluent. Among the above-mentioned methods for wastewater treatments that have drawn attention of 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 initial investment cost and design simplicity [7].

In this study, we have chosen coals from the Baganuur, Nariin Sukhait and Ereen deposits in Mongolia for the preparation of activated carbons. We prepared and characterized different type of coals through activated carbons and evaluated their adsorption capacity. Another objective of the study has been to obtain activated carbon with more surface area using pre-heated water steam and estimate activation characterization by coal rank

MATERIALS AND METHODS

Preparation of activated carbon (Figure 1).

All chemicals used were of analytical grade. The coal samples were from Baganuur, Nariin Sukhait and Ereen deposits in Mongolia. Table 1 shows their basic information. The coal samples were grounded to a size ranging from 1.0 to 1.5 mm and sieved in the mesh. 400 grams of coal samples were purified for 15 minutes by enrichment method using 1000 mL of heavy liquid - ZnCl₂ solution with a density of 1.3 g/cm³ in order to decrease ash content of coal samples. After that, the purified coal samples (light product of enrichment) were pyrolyzed in a laboratory vertical cylindrical retort made of stainless steel, which could contain 1000 g of sample. The retort was placed in an electric furnace (model SNOL) with a maximum temperature of 900°C. A chrome-alumel thermocouple was immersed in the coal bed to measure the actual heating temperature

and equipment for temperature control (potentiometer). The retort was connected with an air-cooled iron tube and water-cooled laboratory glass condenser and a collection vessel for the condensate of liquid product (pitch and pyrolysis water) was used. The non-condensable gases left the system through a thin glass tube using water-cooled condenser. The experiments were carried out at a temperature of 700°C and the heating rate was 20°C min⁻¹ for 2 hours. The yields, including solid residue (coal char), tar and pyrolysis water were determined by weighing, and the yield of gases by the differences measured. Following which carbonized purified coal samples were replaced in quartz tube and flowed with nitrogen to remove the oxygen and heated until 800°C and processed with preheated water steam for 120 minutes [8]. Figure 1 shows the scheme of preparing activated carbon.

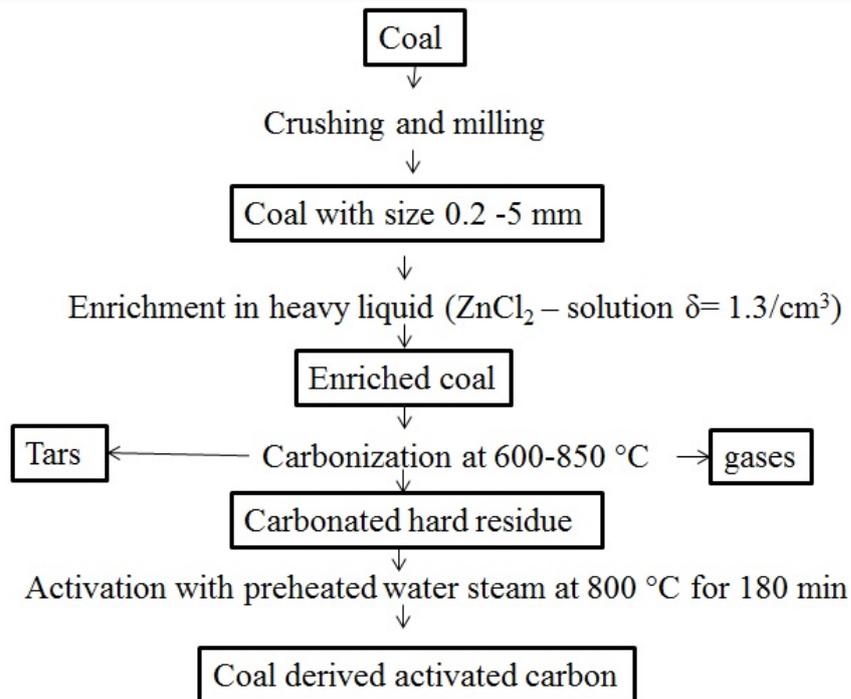


Figure 1. Preparation of activated carbon with preheated water steam

Determination of Iodine number, %

1 g of dried activated carbon was added in to a 250 mL conical flask with 50 mL of 0.1 N iodine solution. The flask was stoppered, shaken for 30 seconds and filtered in funnel with clean filter paper. 50 mL clean filtrate was titrated with 0.1 N sodium thiosulphate

solution until the yellow colour almost disappeared. About 1 mL of starch solution was added and titration continued until the blue indicator colour just disappears. Iodine number X of the carbon was calculated using the following equation.

$$X\% = \frac{(V_0 - V_1) * 0.0127 * 100 * 50}{m * 10} \quad (1)$$

Where: V_1 - volume of sodium thiosulphate solution in mL,
 m - mass of activated carbon in g,

Determination of removal of Methylene blue, mg/g

0.1 g of activated carbon sample was added to a 250 mL conical flask containing 25 mL of methylene blue test solution. The flask was stoppered and shaken until decolourization. When the methylene blue color is completely eliminated, 5 mL of methylene blue solution was once again added and the process was continued until equilibrium. The volume of methylene blue test solution in mL that has just decolourized is the methylene blue value of the activated carbon.

Textural and chemical characterization:

Adsorption characterization for activated carbon obtained from different coals was determined by means of nitrogen adsorption at -196°C using ASAP2010 apparatus (Micromertics). The Brunauer-Emmett-Teller (BET) total surface area and t-method micropore surface area were calculated from the adsorption isotherms using the BET equation and de Boer's t-method. A scanning microscope, equipped with an energy dispersive X-ray microanalysis, was used to determine the surface textural characteristics and elemental composition of activated carbons. 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 plate. The covered time is 60 sec and the gold tin is 5-10 nm.

RESULTS AND DISCUSSION

The results of ultimate and proximate analysis of initial coal samples from Ereen,

Baganuur and Nariin Sukhait deposits are shown in Table 1.

Table 1. Ultimate analysis and proximate analysis of coal samples

Samples	W ^a %	A ^d %	V ^{daf} %	S ^d %	C %	O %	N %	H %
Ereen	6.87	5.9	40.7	0.89	68.9	12.3	1.4	4.9
Baganuur	10.18	13.0	44.0	0.51	58.4	19.8	0.7	4.7
Nariin Sukhait	3.65	7.7	34.0	0.8	68.6	9.1	0.9	4.3

Table 1 shows that the content of ash is higher in Baganuur coal. The content of sulfur is less than 1 in all coals which is good from the environmental point of view. Also the volatile matter is lower in Nariin Sukhait coal, which is a characteristic of a high rank bituminous coal than lignite brown coal of Baganuur and subbituminous middle rank Ereen coal. The content of C is lower and O is higher in the coal

from Baganuur, which is characteristic of oxidized brown coal of lignite type.

In order to investigate the mineral composition of coal samples, pure ashes were obtained after completely burning initial coal samples and their mineral oxide composition was determined by way of X-Ray Fluorescence method, and the results are given in Table 2.

Table 2. Elemental composition of coal ashes

Samples	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Mn ₂ O ₃	Fe ₂ O ₃	CuO	Ratio*
Baganuur	2.66	6.22	24.19	7.23	0.96	40.38	1.18	0.3	17.36	0.11	1.25
Nariin Sukhait	2.5	17.05	22.8	7.3	3.0	14.8	2.7	0.6	27.5	0.07	1.12
Ereen	2.65	14.85	31.62	7.54	1.34	15.5	2.87	0.37	21.74	-	0.83

* $(Fe_2O_3 + CaO + MgO + Na_2O + K_2O) / (SiO_2 + Al_2O_3 + TiO_2)$ acidic < 1 < alkaline

The data in Table 2 show that the main ashes components are SiO₂, Al₂O₃, CaO, Fe₂O₃ in all coal samples. The content of Al₂O₃ is lower in the ash of Baganuur coal and also the SiO₂ is higher in the ash of Ereen coal, the Fe₂O₃ is higher in the ash of Nariin Sukhait coal and also the content of CaO is higher in the ash of Baganuur coal than in other coals. Generally, the major components of activated carbons ash are silicates and aluminates with lesser amounts

of calcium, magnesium, iron, potassium, and sodium. Furthermore, specific ash components like iron, calcium and alkali compounds exhibit a catalytic effect in steam activation, that manifests itself by both an enhanced affinity of the carbonaceous feedstock towards water and by a selective pore formation [9]. The content of Fe₂O₃ in coal ash samples have been confirmed by taking photographs of the ash to show their colored appearance (Figure 2).

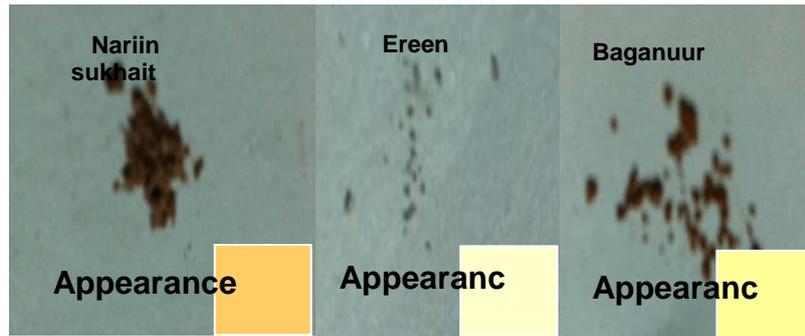


Figure 2. Photographs of the coal ashes

The yellow-red and white-yellow color of ash from Nariin Sukhait and Baganuur coals prove they have higher content of Fe₂O₃. The ratio of (Fe₂O₃ + CaO + MgO + Na₂O + K₂O) / (SiO₂ + Al₂O₃ + TiO₂) in the ash of all coal samples have been calculated. The ratio (Fe₂O₃ + CaO + MgO + Na₂O + K₂O) / (SiO₂ + Al₂O₃ + TiO₂) is more than 1 for the ash from Baganuur and Nariin Sukhait coals and it is less than 1 for the ash from the Ereen coal sample. These results show that the ash of Baganuur and Nariin Sukhait coals have an alkaline and the ash of Ereen coal sample have acidic characters. Alkali compounds like hydroxides

or carbonates of potassium or sodium are known to promote the formation of slit-shaped micropores via intercalation, whereas transition metals and earth alkali compounds enhance mesopore formation via channeling of metallic particles [9].

In order to obtain a good quality adsorbent material with highly developed porosity structure, it is necessary to have additional processing such as, carbonization and activation. For this reason we have purified coal samples by heavy liquid enrichment method (shown in Table 3).

Table 3. The separation in heavy liquid of ZnCl₂ with a density of 1.3 g/cm³

The name of coal deposit	Light product		Heavy product		Initial Ash,%
	Yield,%	Ash, %	Yield,%	Ash, %	
Baganuur	48.49	7.3	44.48	14.2	13.0
Nariin Sukhait	77.4	4.6	14.9	8.9	7.7
Ereen	33.65	3.4	59.51	15.0	5.9

The results of enrichment show that light product is higher in Nariin Sukhait coal and heavy product is higher in the Ereen coal. The light product's ash content decreased almost 2 times in all samples when compared with the

initial samples. After purification, initial coal samples and purified coal samples (light product) were carbonized by the pyrolysis method. (Shown in Table 4).

Table 4. The yields of pyrolysis products of initial and purified coal samples

Samples	Initial samples			Purified samples		
	Hard residue, %	Liquid product,%	Gas, %	Hard residue, %	Liquid product,%	Gas,%
Baganuur	68.31	15.85	15.84	68.5	15.75	15.75
Ereen	68.92	17.06	14.02	69.9	16.2	14.89
Nariin Sukhait	77.95	11.68	10.37	79.6	8.1	13.3

The yield of pyrolysis hard residue (carbonized coal is the main product) is higher for Nariin Sukhait coal, because of its higher rank and more thermostability of organic matter. Therefore, the obtained hard residue (carbonized coal) has a visible porous material with mezo and macro pores. It is possible that some pores are covered (filled in) by volatile matters, which did not leave fully during pyrolysis. The variation of hard residues yield were not observed between purified coal and initial coal.

As mentioned above, samples have been treated with preheated water steam activation (Physical activation) in order to increase the porosity of the pyrolysis hard residue of purified coal. Its technical and physico-

chemical characteristics have been determined through the activated carbon samples obtained by means of physical activation method. The most important technical specification of activated carbons is the adsorption ability, the determination of iodine number and removal of methylene blue by chemical analysis, which are most commonly used and the easiest method for the characterization of activated carbons.

Therefore, obtained activated carbon samples and pyrolysis hard residue samples (without activation) have been tested for iodine number, removal of methylene blue analysis and BET surface area using N₂ gas to evaluate the adsorption ability and the results are given in Table 5.

Table 5. Technical and physico-chemical characteristics of activated carbon employed

Samples	Yield, %	A ^d , %	V ^{daf} , %	Iodine number, %		Removal of MB, mg/g		BET surface area m ² /g		Pore size, nm
				Before	After	Before	After	Before	After	
BN-AC	54.01	14.4	6.0	1.5	14.06	0.6	4.10	0.2	508	0.4
NC-AC	56.6	8.5	3.2	2.6	18.50	1.0	6.30	1.3	442	0.1
E-AC	67.2	8.5	2.9	1.89	11.2	0.48	5.6	0.1	476	0.3

The results of determining the surface area (BET) of initial coal (1) and it's activated carbon (2) samples from the Nariin Sukhait, Ereen, Baganuur coal deposits are given in Table 5. The results show that the surface area of the activated carbon is higher than carbonized coal. This result also evidences that inactivated coal has a smaller surface area and the method of preparing initial coal, including enrichment, carbonization and activation for activated carbon have great influence on the development of porosity structure and surface area.

As seen in Table 5, the determined iodine number of activated carbon of purified and carbonized coals increased 5-17 times and the removal of methylene blue also increased 4-10 times as compared to pyrolysed hard residue samples without activation. BET surface area is higher in BN-AC than E-AC and NC-AC. BET surface area of activated carbons increased as compared to samples without activation. The acativated carbon samples prepared from Ereen and Baganuur coal have higher adsorption ability.

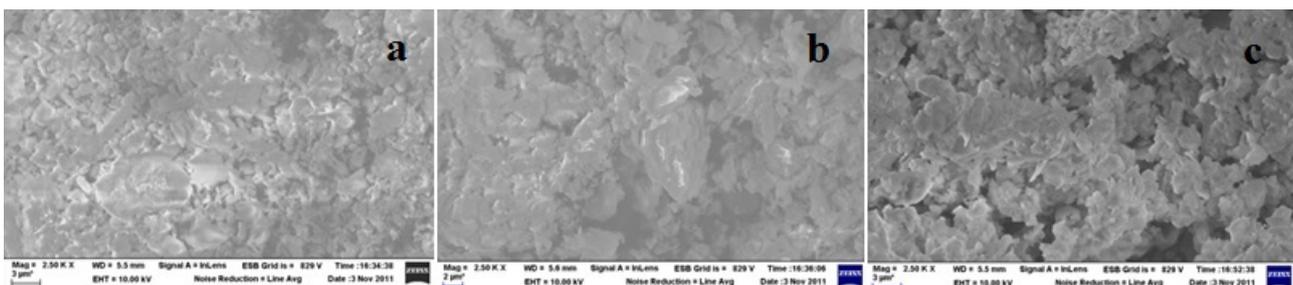


Figure 3. SEM analysis of Activated carbons (a- BN-AC, b- E-AC, c- NS-AC)

The morphology of activated carbon was observed using SEM. Figure 3 shows different views of activated carbons. SEM images of activated carbons show that thick wall opened and a wider porosity is created, thus the external surfaces of activated carbons are full of cavities.

CONCLUSIONS

Proximate and ultimate analysis of and the yields of pyrolysis products show that the Baganuur coal is a low rank oxidized brown coal of lignite type, the Ereen coal is a subbituminous middle rank coal and the Nariin Sukhait coal is a high rank bituminous coal.

According to the results of pyrolysis from purified and initial coal, we have not observed any significant difference in the yield of

Pores of different sizes and shapes can be observed in these figures. But the surface of NC-AC is the smoothest proving that activation was incomplete, primarily perhaps because of the high coal rank, leading to poor evolution of the coal pore structure and to low surface area.

pyrolysis hard residue. Also, The analysis result of technical and physico-chemical characteristics of activated carbon shows that it is possible to prepare more activated carbon with a pore size of 0.4 nm (mesopores) and a surface area of 508 m²/g from Baganuur coal. And, it is possible to produce activated carbon with a pore size of 0.1 nm from Nariin Sukhait coal.

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