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Synthesis and characterization of activated carbon from natural asphaltites

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ABSTRACT

A possibility for utilization of natural asphaltites, based on production of carbon adsorbents, was investigated. Various combinations of physical and chemical activation as well as demineralization procedures were used to obtain final products from natural asphaltites. Carbon adsorbents with developed pore structure and with alkaline character of the surface, as well as tar and gas products, were obtained by water vapor pyrolysis of natural asphaltites. The obtained carbon adsorbents show good adsorption properties; however, this performance is somewhat limited, probably due to their high mineral and sulfur content. It was established that hydropyrolysis is not appropriate method for production of carbon adsorbents on the base of asphaltites from Sirnak deposit due to the material coking. However, a two-stage process, including carbonization and subsequent activation, is appropriate for obtaining of carbon adsorbent with developed pore structure from Sirnak asphaltites. At the same time, hydropyrolysis is suitable for obtaining of activated carbon using asphaltites from Silopi deposit. Different oxygen groups were detected on the activated carbon surface, and their effect on surface properties of the samples was discussed.

1. Introduction

Activated carbons are excellent adsorbents due to their high surface area, dominantly microporous texture, high surface reactivity and high concentration of active sites, represented by chemical surface groups containing oxygen or another heteroatom [1]. These adsorbents have variety of applications in food industry, pharmaceutical, chemical, petroleum, nuclear, automobile and vacuum industries. Activated carbon are also used for removal of organic pollutants (phenols, naphthalene, trihalomethanes, etc.) and metal ions from water, purification of waste solutions, separation, decolourization, deodorization, dechlorination, filtration of gases and liquids, concentration of traces of elements and radioactive isotopes, production and analysis of high purity substances, etc. [1–3].

Despite many advantages of activated carbons, they have few drawbacks. For example, the price of activated carbons is considerably high due to intensive energy cost during their production.

Literature survey indicates that activated carbons can be prepared from a variety of raw materials such as lignites, polymers, sugar, wood, biomass, fruit stones and shells—apricot stones, olive stones, peach stones, almond stones, grape seeds, bean pods, corn cobs, coconut shells, etc. [4–17]. The adsorptive capacities of these activated carbons are usually comparable to these of commercial activated carbons.

Usually, there are two steps for preparation of activated carbons. The first stage is the carbonization of the precursor, and the second stage is the activation of the solid product after carbonization. Usually, the physical activation is carried out in the presence of suitable oxidizing gases such as water vapor, CO_2, etc. In this research, a new one-step pyrolysis technology (in the presence of water vapor) was applied. The chemical activation is performed with different chemical activating agents—K_2CO_3, KOH, $ZnCl_2$, H_3PO_4, etc. Once the chemical agent is eliminated during heat treatment, the porosity of the final product is much more developed [18,19]. By applying physical and chemical activation, it is possible to produce activated carbon with a high surface area and with well-developed microporosity.

In some papers, the term ‘asphaltites’ is used for petroleum tar pitches [20,21]. However, in this study the term ‘asphaltites’ indicates the deposits of natural fossil materials. These natural asphaltites contain dark-colo‘solid petroleum’ with high softening point as well as high amounts of volatile substances (petroleum), which can be used as solid fuel (limited use due to high sulfur content). The soluble fractions from asphaltites can be used as liquid fuel. The melting point of natural asphaltites is in the range 200–315 °C. They contain mainly hydrocarbons ($C < 18$) as well as some polar compounds, and almost no oxygenated compounds [22]. Natural asphaltites are also characterized by high sulfur and ash content, due to presence of clay minerals, quartz, albite, orthoclase, pyrite, calcite, dolomite, Mo, V, Ni, Ti, Al, Si, Fe, Cu, Ca, U, etc. [22–24]. Natural asphaltites and other sources of asphaltic materials are considered to be formed by migration of petroleum and its solidification in the cracks during tectonic movements, followed by alteration in composition, due to the loss of lighter fractions as well as biodegradation, oxidation and other chemical reactions, which increase the molecular weight and C/H atomic ratio [25].

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Natural asphaltites contain 1–5.3% (wt.) total moisture, 33–45% ash, 4.1–6.4% sulfur, 24–40% volatile matter, 47–59% fixed carbon and 3.2–5.6% hydrogen [22]. Due to their high sulfur content, their use as a fuel without any physical or chemical cleaning procedures can create serious environmental pollution. During the process of burning, considerable amounts of carbonates (calcite and dolomite), in the composition of the precursor can produce CO_2 after thermal degradation.

Natural asphaltites can be converted by pyrolysis into a variety of secondary products such as gas (light hydrocarbons) and tar [22]. Natural asphaltites can be subjected to liquefaction to produce synthetic fuels [26–28] as well as precursor for high-tech carbon materials—carbon fibres [29–31], carbon foam [31], etc. Asphaltites could also be used as a precursor for trace metals and for production of ammonia.

As far as we know, studies concerning production of activated carbon from natural asphaltites are almost absent—we have not found any reference in the literature. At the same time, the natural asphaltites have found limited use—e.g. they are trying to use them in some power plants in Turkey as a fuel alternative to coals.

The aim of this paper is to investigate the possibilities to obtain activated carbons from natural asphaltites by different methods – water vapor pyrolysis, pyrolysis and subsequent physical or chemical activation – and to investigate their physical characteristics, surface chemistry.

2. Materials and methods

There are many very rich deposits of natural asphaltites in Southeastern Turkey with total capacity of around 8.10^7 t [22,29]. Our study is focused on three natural asphaltite samples from two deposits in Turkey—one sample from Sirnak deposit and two samples from Silopi deposit. All natural asphaltite samples were dried, milled and sieved. The fractions with particle size 1–3 mm were selected for pyrolysis.

Demineralization and depyritization procedures were applied in order to decrease ash content and to obtain asphaltites without inorganic sulfur. Demineralization of Sirnak asphaltite sample was carried out by modified Radmacher method—consecutive treatment with 5% HCl, 50% HF and 35% HCl at ambient temperature [32,33].

A depyritizated sample was also prepared from Sirnak asphaltite samples. For this purpose, the initial natural asphaltite was treated by 17% HNO_3 for 3 h at ambient temperature [33–35]. Mineral acids treatments for demineralization and depyritization are followed by comprehensive washing with distilled water until pH 7 is reached. The pyritic sulfur (S_p^{db}) of this sample was reduced from 0.37% down to 0.02%. Technical analysis data of initial, demineralized and depyritized samples are presented in Table 1.

2.1. Preparation of carbon adsorbent by water vapor activation

A two-stage process, which includes carbonization (step 1) and physical activation by water vapor (step 2), was carried out for the initial Sirnak asphaltite sample. After the first step, carbonization, a dense monolithic char was produced. In order to obtain effective treatment for this sample, the solid product after carbonization was crashed and milled, and then subjected to water vapor pyrolysis. Carbonization process was carried out at 600 °C for 10–15 min, with product yield 75–80%. The next activation stage by water vapor was performed at 800 °C for 60 min.

Table 1
Technical analysis of natural asphaltites, in wt.%.

Sample	Moisture W^a	Ash A^{db}	Total sulfur content S_t^{db}
IASir	0.77	44.76	5.72
DemASir	0.90	20.41	5.06
DepASir	0.86	27.98	5.29
IASil-1	0.96	36.90	4.78
IASil-2	0.92	35.95	7.04

a—analytical basis; db—dry basis; t—total; IASir—initial Sirnak asphaltite sample; DemASir—demineralized Sirnak asphaltite sample; DepASir—depyritized Sirnak asphaltite sample; IASil-1—initial Silopi-1 asphaltite sample; IASil-2—initial Silopi-2 asphaltite sample.

The initial asphaltite Silopi-1 and Silopi-2 samples were subjected to one-stage carbonization and subsequent activation process by water vapor at 800 °C for 30 min.

2.2. Preparation of carbon adsorbent by chemical activation

A chemical activation by K_2CO_3 was carried out by using impregnation method. K_2CO_3 was selected among other activation agents like $ZnCl_2$, H_3PO_4, KOH, NaOH, etc., because it is not harmful and it is even used as food additives. The conditions of the chemical activation procedure were selected on the base of our previous study [21]. First, the activating agent and the natural asphaltite sample were mixed in weight ratio 1:1. After drying the water from the reaction mixture at 110 °C, the obtained material was subjected to carbonization at 950 °C for 5 min in a muffle furnace under nitrogen atmosphere. After cooling the solid product after carbonization was washed subsequently several times with hot distilled water and finally with cold distilled water to remove the impurities. The washed sample was dried at 110 °C to obtain chemically activated carbon. The process of chemical activation does not necessitate additional grinding after impregnation.

2.3. Characterization of the samples

The porous structure was studied by N_2 adsorption at 77 K using Quantachrome NovaWin2 porosimeter. The amount of oxygen-containing functional groups with increasing acidity on the carbon surface was determined applying Boehm's method by neutralization with basic solutions of increasing strength—$NaHCO_3$ (for carboxylic groups), Na_2CO_3 (for lactonic groups), NaOH (for phenolic groups) and EtONa (for carbonyl groups). About 0.5 g (±0.0001 g) of the carbon was put in contact with 100 mL of 0.05 N basic solution in sealed flasks. The suspensions were shaken at least 16 h and then filtered. The excess of base remaining in the solution was determined from back-titration after adding an excess of standard HCl solution [36]. It was assumed that $NaHCO_3$ was capable of neutralizing all carboxylic groups, Na_2CO_3—carboxylic and lactonic groups; NaOH—carboxylic, lactonic and phenolic groups; and sodium ethoxide was assumed to neutralize all acidic groups. The amount of basic sites was determined with 0.05 M HCl [37]. The pH of the carbons was measured according to the following procedure: 4.0 g of carbon was weighed into a 250-mL beaker, and 100 mL water was added. The beaker was covered with a watch glass, and the mixture was boiled for 5 min. The suspension was set aside, and the supernatant liquid was poured off at 60 °C. The decanted portion was cooled down to ambient temperature and the pH was measured to the nearest 0.1 pH unit.

3. Results and discussion

The technical analysis of the initial, demineralized and depyritized samples of natural asphaltites is shown in Table 1. It should be noted that all the initial samples are characterized by very high mineral content, especially the sample from Sirnak deposit. The sulfur content of the samples is also high, as it is the highest for sample from Silopi-2 deposit. As expected, the results show that demineralization reduces the mineral content, and the depyritization decrease the sulfur content.

On the other hand, natural asphaltite samples from Silopi deposit demonstrated low coking ability, which allows one-stage process of simultaneous carbonization and activation to be performed in this case. The yields of produced oils (liquid product) and activated carbon (solid product) as well as the determined adsorption capacity towards iodine, are shown in Table 2.