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Preparation and surface characterization of activated carbons from *Euphorbia rigida* by chemical activation with $ZnCl_2$, K_2CO_3, NaOH and H_3PO_4

Murat Kılıç, Esin Apaydın-Varol, Ayşe Eren Pütün*

Department of Chemical Engineering, Faculty of Engineering and Architecture, Anadolu University, Eskişehir 26480, Turkey

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ABSTRACT

Preparation of activated carbons from *Euphorbia rigida* by chemical activation with different impregnation agents and ratios was studied. $ZnCl_2$, K_2CO_3, NaOH and H_3PO_4 were used as chemical activation agents and four impregnation ratios (25–50–75–100%) by mass were applied on biomass. Activation is applied to impregnated biomass samples at 700 °C under sweeping gas in a fixed bed reactor. For determination of chemical and physical properties of the obtained activated carbons; elemental analysis was applied to determine the elemental composition (C, H, N, O) and FT-IR spectra was used to analyze the functional groups. BET equation was used to calculate the surface areas of activated carbons. For understanding the changes in the surface structure, activated carbons were conducted to Scanning Electron Microscopy (SEM). Maximum BET surface area (2613 m^2/g) was reached with 75% K_2CO_3 impregnated biomass sample. Experimental results showed that impregnation types and ratios have a significant effect on the pore structure of activated carbon and *E. rigida* seems to be an alternative precursor for commercial activated carbon production.

1. Introduction

Activated carbon, an adsorbent with its large porous surface area, controllable pore structure, thermo-stability and low acid/base reactivity is currently receiving great attention, owning to its superior and efficient ability in air pollution control, solvent recovery, food processing, chemical and pharmaceutical industries, wastewater treatment (dyes, heavy metals, detergents, herbicides, pesticides and polyaromatic hydrocarbons), metal recovery, catalysis as well as in improving odor and taste [1].

Production of activated carbon can either be through physical or chemical activation. The nature of the precursor, activation method, and activation conditions determined the characteristics of porosity in activated carbons, including pore size distribution, shapes of the pores, and surface chemistry [2]. Physical activation is a two-step process [3]. The material is carbonized under inert atmosphere and then activated at high temperature using either steam or carbon dioxide as the activating reagent to produce more porous structures [4]. In chemical activation, raw material is impregnated with an activation reagent and heated in an inert atmosphere. The carbonization step and the activation step proceed simultaneously. By dehydration and oxidation reactions of the chemicals, pores are developed. Produced char then washed to rid it from residual impurities [3]. The advantages of chemical activation are: its low energy and operating cost, higher carbon yields and large surface areas when compared with physical activation. Chemical activation also has better development of porous structure [4,5]. Knowledge of different variables during the activation process is very important in developing porosity of carbon which is sought for given applications. Chemical activation is held in the presence of dehydrating reagents such as KOH [6], K_2CO_3 [7], NaOH [8], $ZnCl_2$ [9], H_3PO_4 [10] and H_2SO_4 [11] which influence pyrolytic decomposition and inhibit tar formation [12]. These reagents can improve the pore distribution and increase the surface area of adsorbents [13].

Activated carbons are produced from a variety of carbonaceous materials. The choice of precursor largely depends on its availability, cost, and purity, but the manufacturing process and intended application of the product are also important considerations [5]. Therefore evaluation of biomass is getting increased attention all over the world as it is renewable, widely available, cheap, and environmental friendly [14]. There are a number of biomass sources, such as forest residues, low grade plants, agricultural residues and municipal solid wastes, which can be utilized for activated carbon precursor. One of them is *Euphorbia rigida* (*E. rigida*), a large genus of the *Euphorbiaceae*, a family of laticiferous herbs, shrubs and small trees, distributed in the tropical and warm temperature regions of the world. Many of the species are succulent and inhabit dry places. About 2000 species have been reported throughout the world, chiefly in tropical regions. It is known that 80 species of *Euphorbia* are found in Turkey [15]. In Turkey *E. rigida* grows on the

* Corresponding author. Tel.: +90 222 335 0580x6504; fax: +90 222 323 9501.
E-mail address: aeputun@anadolu.edu.tr (A.E. Pütün).

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arid lands of Middle Anatolia in abundant quantities and without any requirement of special labor, this has made this plant attractive as a new source [16].

The aim of the present work is to produce high surface area activated carbon from *E. rigid*a by chemical activation using different impregnation agents and ratios. The influence of different impregnation agents and ratios on surface chemistry was determined using instrumental methods such as elemental analysis, FT-IR, BET and SEM.

2. Materials and methods

2.1. Precursor preparation

E. rigida was collected from southwest Anatolia. It was harvested between May and July, dried at room temperature. Drying was timed up to obtaining a constant weight. After drying raw material was ground in a high-speed rotary cutting mill and stored in a cool and dark room. Bulk density of 243 m^3/kg and a particle size in the range from 0.425 to 1.80 mm was used for preparation of activated carbon.

2.2. Activation method

Raw material was directly impregnated with chemical activation agents. Ground and sieved *E. rigida* were treated with $ZnCl_2$, K_2CO_3, NaOH and H_3PO_4 solutions at room temperature in four different weight ratios as 25–50–75–100%. Continuous mixing of the precursor with chemicals for 24 h was maintained by using a magnetic stirrer. After mixing, solutions were allowed to dry at room temperature for 24 h and then dried at 85 °C for 72 h in a temperature controlled oven to prepare impregnated samples. After this period, impregnated samples were ready for the carbonization and activation which were carried out simultaneously.

Impregnated samples than carbonized in a stainless steel fixed bed reactor at 700 °C under nitrogen (N_2) flow of 100 cm^3/min and at a heating rate of 10 °C/min and held at this temperature for 1 h. After being cooled, all the carbonized samples were washed several times with hot water until pH became neutral and finally washed with cold water to remove residual chemicals. Washed samples were dried at 105 °C for 24 h to obtain the final activated carbons. The samples and activated carbons were classified as ER_Z, ER_K, ER_N, ER_H, and AC_Z, AC_K, AC_N, AC_H. The first two characters, ER, represent *E. rigid*a, and AC, represents activated carbons, the third characters, Z, K, N and H, represents $ZnCl_2$, K_2CO_3, NaOH and H_3PO_4 impregnation, respectively.

2.3. Characterization of impregnated samples and activated carbons

Yield is usually defined as final weight of activated carbon produced after activation, washing, and drying, divided by initial weight of raw material; both on a dry basis. The following relationship is used for calculating the yield of activated carbons:

$$\text{Yield}\,(\%) = \frac{W_{ac}}{W_i} \times 100 \quad (1)$$

where W_i is mass of impregnated sample and W_{ac} is mass of the dried carbon after washing [5,7].

Surface areas of each activated carbon were calculated from N_2 adsorption isotherms by using BET (Brunauer–Emmett–Teller) method with Quantachrome Autosorb 1 analyzer. The adsorption data of the total pore volume (V_{total}) were determined from the amount of nitrogen adsorbed at a relative pressure of 0.995 and calculated with the manufacturer's software. The same adsorption data were also used for calculation of the micropore volume by the *t*-plot method. The mesopore volume (V_{meso}) was calculated by subtracting V_{micro} from V_{total} ($V_{meso} = V_{total} - V_{micro}$).

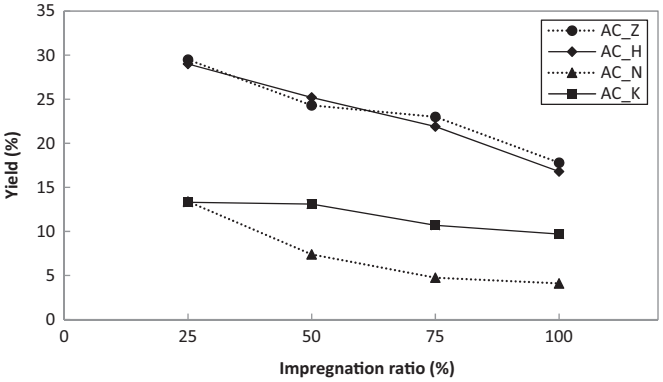

Fig. 1. Effect of impregnation type and ratio on the yield of activated carbons.

The activated carbons were analyzed for carbon, nitrogen, hydrogen and oxygen (by difference) contents using Carlo Erba EA 1108 elemental analyzer. A qualitative analysis of activated carbons was conducted by FT-IR transmission spectra using Bruker Tensor 27 analyzer in wave number range of 4000–400 cm^{-1}. The samples were well mixed with potassium bromide at a ratio of 1:99 and the mixture was pressed into pellets to be used in the analysis.

SEM images were recorded by using Zeiss EVO 50 Scanning Electron Microscope. Samples were placed on carbon bands and coated with a thin layer of gold–palladium in an argon atmosphere using Agar Sputter Coater.

3. Results and discussions

Table 1 shows the ultimate and proximate analysis results of precursor. A high carbon and low ash content of *E. rigida* indicates that the precursor is suitable for activated carbon production. Fig. 1 shows the yields of the activated carbons obtained using different chemical agents and ratios. The yields of activated carbons were in the range of 29.5–17.8% for $ZnCl_2$, 13.3–9.7% for K_2CO_3, 13.4–4.1% for NaOH, and 29.0–16.8% for H_3PO_4 impregnated samples. It is shown that yield of carbon decreases as the impregnation ratio increases, because of promoting the gasification of char and increasing the total weight by excess chemicals. Granular activated carbons were obtained by activation of $ZnCl_2$ and H_3PO_4 impregnated samples and powdered activated carbons were obtained by activation of K_2CO_3 and NaOH impregnated samples.

Adsorption behavior and pore structure of activated carbons can be analyzed by using Nitrogen adsorption isotherms. General properties of activated carbons can be explained by the shape of these isotherms. Fig. 2 shows the N_2 adsorption-desorption isotherms of

Table 1
Proximate and ultimate analyses (wt.%) of *E. rigid*a (as received).

Proximate analysis (%)	
Moisture	3.0
Ash	6.4
Volatiles	76.8
Fixed C	13.8
Ultimate analysis (%)	
C	49.56
H	5.16
N	1.20
O[a]	44.08
H/C	1.24
O/C	0.67
HHV (MJ/kg)	16.26

[a] By difference.