Original Research Paper

Novel and sustainable precursor for high-quality activated carbon preparation by conventional pyrolysis: Optimization of produce conditions and feasibility in adsorption studies

Hasan Saygılı [a,*], Fuat Güzel [b]

[a] Department of Petroleum and Natural Gas Engineering, Faculty of Engineering and Architecture, Batman University, 72100 Batman, Turkey
[b] Department of Chemistry, Faculty of Education, Dicle University, 21280 Diyarbakır, Turkey

ABSTRACT

The purpose of this study is to produce powdered activated carbon under optimized conditions from a novel precursor, carob (*Ceratonia siliqua* L.) industrial processing residues, by zinc chloride ($ZnCl_2$) chemical activation. The production influences of impregnation ratio ($ZnCl_2$/precursor, g g^{-1}), carbonization temperature, and carbonization duration on the some textural properties of produced carbons have been investigated and the best production conditions were determined. The optimum conditions resulted in an activated carbon with a carbon content of 58.95% and a yield of 48.83%, while the surface area of 1693 m^2 g^{-1}, with the total pore volume of 2.655 cm^3 g^{-1}, mesoporosity of 98.95% and average pore diameter of 6.70 nm. Its adsorptive performance was tested using methylene blue and metanil yellow dyes. The adsorption behaviors for both dyes were well described by the Langmuir isotherm model, showing a monolayer adsorption capacity of 597 mg g^{-1} and 568 mg g^{-1}, respectively. The results indicate that optimal activated carbon could be employed as an efficient adsorbent for the removal of the basic and acidic dyes from effluents.

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1. Introduction

In the last decade, application fields of the porous materials are rapidly increasing. Activated carbons (ACs) are the most important member of the porous materials. ACs in the porous have gained much attention due to their large surface area, well-developed porosity, various oxygen-containing functional groups on the surface, good chemical stability, good corrosion resistance, good electrical conductivity and relatively high mechanical strength [1,2]. These excellent features have made it widely used on the industrial scale as a material for the purification and separation processes [3], as a catalyst or a catalyst support in the catalytic processes [4,5], gas storage [6,7], electrode materials in electrochemical devices and processes [8,9], and so on. Due to its multipurpose applications, the demand of ACs is growing in many countries. Recently, increasing worldwide environmental concern is also driving the demand for ACs which, according to recent reports, is expected

to grow at the compounded annual growth rate of more than 13% by 2017 [10].

The physical and chemical properties of ACs depend on the activation methods as well as the properties of the precursor [11]. In principle, in their production, two methods such as physical activation and chemical activation are used. Chemical activation has been object of significant research in the recent years, as it offers several advantages compared to the so-called physical activation, e.g., lower temperatures for pyrolysis, high yield, very high surface area, etc. Among the disadvantages of the chemical activation process, the corrosiveness of the process and the washing stage are to be noted. The chemicals such as alkali (KOH, K_2CO_3, NaOH and Na_2CO_3), alkali earth metal salts ($AlCl_3$ and $ZnCl_2$) and some acids (H_3PO_4 and H_2SO_4) are widely used for chemical activation. These chemicals are dehydrating agents that influence pyrolytic decomposition and inhibit the formation of tar [11–13]. $ZnCl_2$ is an activation agent that results in a high yield and a high surface area, and thus is widely used in the chemical activation method [13,14]. It also provides the advantage of easy recovery by washing with water.

Commercial activated carbons have some disadvantages. In particular, it is quite expensive, and the higher the quality, the greater

* Corresponding author.
  E-mail addresses: hasan.saygili33@gmail.com (H. Saygılı), fguzel@dicle.edu.tr (F. Güzel).

the cost. The regeneration of saturated carbon with any substance by thermal and chemical procedure is also expensive, and results in loss of the adsorbent. This has led many researchers to find a more economic and efficient adsorbents. ACs can be manufactured virtually from any carbonaceous precursor, but the most commonly used precursors are coals, polymers, carbon nanofibers and nanotubes, lignocellulosic materials. It is well known that lignocellulosic materials are investigated vastly as precursors in recent years due to their distinct advantages, such as renewable, cheaper, environmentally friendly and huge amount [2]. A large number of agricultural by-products have been successfully converted into low-cost ACs. According to our literature knowledge, there is no information related to the utilization of carob processing residues (CR). They are either disposed in nature or utilized as fertilizers and solid fuel at best in Turkey. Releasing in nature of these wastes, which cause storage challenges, is the likely brings various environmental troubles.

The main purpose of the present work is to determine the optimal conditions to produce AC with high surface area mesoporous from CR by $ZnCl_2$ activation. The effects of some main production parameters, including impregnation ratio (IR) ($ZnCl_2$/CR, g g^{-1}), carbonization temperature (CT) and carbonization duration (CD) on pore structure of the produced ACs were also discussed. Moreover, the AC (CAC) produced at optimized conditions was characterized with various physicochemical techniques such as proximate analysis, ultimate analysis, pore structure analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD) and surface functional group analysis by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Boehm's titration method and point of zero charge (pH_{pzc}). In addition, the CAC was tested to remove cationic and anionic dyes from aqueous solutions.

2. Materials and methods

2.1. Materials

CRs were obtained from a local food processing factory in Adana, Turkey. They were washed with water to take off impurities and subsequently air dried. Thereafter, CRs were smashed and sieved to a desired particle sizes between 1 and 2 mm prior to its chemical activation. $ZnCl_2$, basic dye MB (Type: cationic, chemical formula: $C_{16}H_{18}ClN_3S$, M_w: 319.85 g mole^{-1}, color index: basic blue 9, λ_{max}: 665 nm), acidic dye MY (Type: anionic, chemical formula: $C_{18}H_{14}N_3NaO_3S$, color index: acid yellow 36, λ_{max}: 433 nm, M_w: 375.38 g mole^{-1}) and other used chemicals were purchased from Sigma-Aldrich Co. (Ankara, Turkey). All the chemicals used were of analytical grade.

2.2. Production studies of optimal activated carbon

The optimal conditions for AC production from CRs were determined by examining effects of the IR (1:1, 2:1, 4:1, 6:1 and 8:1; $ZnCl_2$/CR, g g^{-1}), CT (400, 500, 600 and 800 °C) and CD (0.5, 1.0, 2.0 and 4 h) (Table 1). These processes were performed by heating in a horizontal stainless-steel tubular reactor (7.0 cm diameter ×100 cm length). At every turn, 50 g of the dry sample impregnated with $ZnCl_2$ was placed into the reactor and nitrogen gas was passed through at a flow rate of 100 mL min^{-1}; the system was heated at a rate of 10 °C min^{-1}. the produced ACs were cooled down to room temperature under nitrogen flow, and 0.2 N HCl was added onto their, and were washed sequentially several times with hot distilled water to remove residual chemical until it did not give Cl$^-$ reaction with AgNO$_3$, and dried at 105 °C for 12 h and then sieved between 177 and 420 μm. They were referred to as AC followed by the IR, CT and CD; for instance, AC11405 represented IR 1:1 for the first two numbers of 11, CT of 400 °C for the third number of 4, and CD for 0.5 h for last 05. The $ZnCl_2$ exerted for the chemical activation is recovered from the wash water, and used again in subsequent experiments. The yield of optimal AC was calculated as the ratio of the dry weight of produced AC to the weight of the air-dried of the precursor.

2.3. Characterization

The advantage of the CR for AC production was first checked using various methods such as elemental composition, proximate and component analyses. Elemental composition of materials (carbon, nitrogen, hydrogen, and sulfur) was determined by using the LECO CHNS-932 elemental analyzer. The proximate analysis was conducted according to ASTM D 3172-3175 test standards and the results were given as moisture, volatile matter, ash, and fixed carbon contents. Similar analyses were performed for the AC produced at optimized conditions. Biochemical component analysis including extractives, lignin, hemicelluloses, and cellulose of CR was done according to Technical Association of the Pulp and Paper Industry, (TAPPI) standards; T264 om-88, T222 om-88 and T203 om-83, respectively. The thermal characteristic was measured with TG analyzer (Shimadzu, TGA/DTA-50). About 10 mg of sample material was heated from 30 °C to 1000 °C at a ramping rate of 10 K min^{-1} under N_2 gas atmosphere with the low rate of 200 mL min^{-1}, until no further weight loss was detected.

SEM apparatus (JEOL JSM- 6335F) was used to study the surface morphology and the porosity. Crystallographic characterization was examined by XRD measurement performed on a Bruker D8 Discovery EVA diffractometer using monochromatic copper radiation (Cu Kα, λ = 0.1541 nm) at 40 kV and 40 mA over the 2θ range 0–80°. The pore characterization of the CR-derived activated carbons relating to surface area, pore volume and pore size distribution was carried out by measuring nitrogen (N_2) adsorption-desorption isotherms at −196 °C on an automatic apparatus (Micromeritics, ASAP2020). The BET surface area (S_{BET}) was determined based on the standard Brunauer–Emmett–Teller multipoint method in the region of relative pressures (0.05–0.35) near completed monolayers. The pore size distribution of the samples was obtained according to the Barrett-Joyner-Halenda (BJH) method. The total pore volume (V_T) was calculated from the amount of nitrogen adsorbed at $P/P_0 = 0.99$. The micropore volume (V_{mic}) was obtained by t-plot method. The mean pore size (D_P) was calculated according to the Eq. (1).

$$D_P = \frac{4V}{S_{BET}} \tag{1}$$

The microporosity (V_{mic} (%)) ($V_{mic}/V_{tot} \times 100$) and mesoporosity ($V_{mes}$(%)) ($100 − V_{mic}$(%)) of produced ACs were determined based on the volume of total pore. Prior to the measurement, the samples were first outgassed under vacuum at 300 °C for 5 h to remove any adsorbed moisture and/or gases.

Surface functional groups were detected using the pressed potassium bromide (KBr) pellets containing 5% of carbon sample by FT-IR spectrometer (Perkin Elmer spectrum 100) in the scanning range of 4000–650 cm^{-1}. The surface atomic compositions measured by using a Thermo K-Alpha spectrometer with a monochromic Al Kα source at 1486.7 eV, with a voltage of 15 kV and an emission current of 10 mA. The surface oxide functional groups/sites were determined by the Boehm method. For that purpose, about 0.15 g of CAC was placed in 25 mL of the following 0.05 M solutions: sodium hydroxide, sodium carbonate and sodium bicarbonate. The solutions were shaken for 24 h and then 5 mL of each filtrate was pipetted and excess of base was titrated with standard HCl. The number of various types of acidic groups/sites was calcu-