



Influence of activation atmosphere used in the chemical activation of almond shell on the characteristics and adsorption performance of activated carbons



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ARTICLE INFO

Article history:

Received 18 April 2013

Received in revised form 3 September 2013

Accepted 29 October 2013

Available online 22 November 2013

Keywords:

Activated carbons

Activation atmosphere

Chemical activation

Adsorption

Air pollution control

Agricultural waste

ABSTRACT

The aim of this work was to compare the effect of different activating atmospheres on the final properties and adsorption performance of activated carbons. Almond shell based activated carbons have been obtained by chemical activation with phosphoric acid. Two sets of activated carbons were prepared. First set was prepared under inert atmosphere at different impregnation ratios, temperatures and times of activation. Second set of activated carbons was prepared at the same activating conditions except the activating atmosphere using an oxidant one. Activated carbons prepared under both activation atmospheres were characterized by elemental analysis (EA), thermogravimetry (TGA), temperature programmed desorption (TPD), point zero charge (PZC), Boehm titration and N₂ physisorption. To study the adsorption performance of the activated carbons toluene adsorption–desorption isotherms were determined gravimetrically. The results obtained confirm that the activating atmosphere has a strong influence on the final characteristics of the activated carbons. Activated carbons with higher oxygen content and more negative surface charge have been obtained by changing the activating atmosphere by an oxidant one. Surface area is also higher for activated carbons prepared under oxidant atmosphere. However toluene adsorption capacity is lower for activated carbons prepared under oxidant atmosphere due to their surface chemistry.

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1. Introduction

Activated carbons are one of the most versatile adsorbents to be used for the effective removal of volatile organic compounds in gas streams [1]. The adsorption capacity of an activated carbon depends on the porosity [2,3], mainly on the microporosity, and on the surface chemistry [4].

Depending on the characteristics of the adsorbates, activated carbons can be designed by using the appropriate precursor and optimizing the preparation conditions; this is known as the tailoring concept [5]. Main parameters affecting the characteristics of activated carbon are impregnation ratio, activation temperature, activation time and activating atmosphere.

Activated carbons can be produced from a large variety of raw materials by chemical or physical activation [6]. Advantages of the chemical activations compared to the physical activation are the lower activation temperature and the shorter activation time. The chemical activation involves the impregnation of the raw material with a chemical agent and the heat treatment of the mixture to carbonize the material. Different activated agents can be used in the chemical activation but

phosphoric acid permits the preparation of activated carbons with lower activation temperatures [7,8]. Phosphoric acid promotes the depolymerization, dehydration and redistribution of constituent biopolymers [9] during the pyrolytic decomposition of lignocellulosic materials.

Activated carbons with a large development of porosity can be prepared from lignocellulosic wastes by chemical activation with phosphoric acid [10–14].

The preparation of activated carbons by chemical activation with phosphoric acid under inert atmosphere, usually N₂, has been studied by several authors [8,11,15–17]. Although the effect of the phosphoric acid on the activation of activated carbons is well defined, the effect of the atmosphere during the heat treatment has only been studied by few authors [18–21].

Puziy et al. [12] obtained activated carbons with a higher oxygen content when an air atmosphere is used instead of N₂ atmosphere. Porosity of activated carbons is also affected by the activating atmosphere; the use of an oxidant atmosphere instead of an inert atmosphere produces activated carbon with larger surface areas [12,19–22] and an increase in mesopore volume [21,23] due to the widening of the pores during the activation process. It can be explained in terms of the aromatization process during heat treatment. The presence of oxygen inhibits the aromatization process, reducing the influence of the phosphoric acid in both promoting

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the development of porosity and reducing the extent of contraction produced during the heat treatment [18].

The present work compares the characteristics of activated carbons obtained by chemical activation of almond shells as well as their toluene adsorption performance of two series of activated carbons prepared with the same activation conditions except the activating atmosphere: either under N₂ or 8% O₂/N₂ atmosphere.

2. Materials and methods

2.1. Preparation of activated carbons

Raw material chosen for the preparation of activated carbons was almond shell from Vera del Moncayo, Zaragoza (Spain). Dry shells were crushed and sieved at 0.2–1 mm. The chemical activation was carried out by impregnation of the almond shell with (ortho)-phosphoric acid of 89 wt.% followed by one-step carbonization-activation under N₂ or in 8% O₂/N₂ atmosphere.

Impregnation ratio (defined as weight of phosphoric acid/weight of precursor), activation temperature and activation time were selected according to a previous work [15]. In that work, a total of 12 activated carbons were prepared under N₂ atmosphere. The activation conditions which led to activated carbons with higher toluene adsorption capacities [24] were selected to prepare the new activated carbons under 8% O₂/N₂ activating atmosphere.

Before activation, the almond shell is mixed with a determined amount of phosphoric acid of 89 wt.% concentration to reach the impregnation ratios in the range 0.5–1.5. The suspension was shaken at room temperature during 1 h. The impregnated samples were further thermally treated at different activation temperatures under a flow of 250 cm³/min either of 8% O₂/N₂ (which was kept during both heating and cooling), and maintained at the selected temperature during a time ranging from 30 to 120 min. Solid pyrolysis residues were water washed in Soxhlet until pH >6. The resulting activated carbons were dried at 100 °C until constant weight and stored under Ar.

The activated carbons included in this study are given in Table 1.

2.2. Characterization of activated carbons

Activated carbons were characterized by elemental analysis, thermogravimetry (TGA) temperature programmed desorption coupled to mass spectrometry (TPD-MS), point of zero charge (PZC), Boehm titration and nitrogen adsorption at –196 °C.

Ultimate analysis of the activated carbons was carried out in a Thermo Flash 1112 microanalysis apparatus. Oxygen content was obtained by difference.

Thermogravimetric (TG) curves were obtained in a TA Instruments thermobalance. Approximately 20 mg of sample was placed in a Pt crucible and was heated at 10 °C/min up to 1000 °C under a flow of Ar.

The TPD runs were carried out with a custom built set-up, consisting of a tubular quartz reactor placed inside an electrical furnace connected

to a quadrupole mass spectrometer from Pfeifer. TPD experiments were carried out by heating the samples in Ar flow up to 1100 °C at a heating rate of 10 °C/min, and recording the amount of CO and CO₂ evolved at each temperature with the mass spectrometer. The calibrations for CO and CO₂ were carried out by standards diluted in Ar. For each experiment 0.5 g of activated carbon was placed in a horizontal quartz tube reactor under a stream of 30 ml/min of Ar.

The immersion technique [25] was used to determine the point of zero charge of the samples. Suspensions of 0.7 g of activated carbon were put in contact with 10 ml of NaNO₃ 0.1 M at different pH values. Initial pH values were obtained by adding an amount of HNO₃ or NaOH solution taking the NaNO₃ solution to pH ≈ 3, pH ≈ 6 and pH ≈ 10. The suspensions were agitated for 24 h in a shaker at 250 rpm at room temperature and filtered. The pH of the filtered solutions was measured. The final values for the PZC were the average of the three pH values.

The selective neutralization method was used to evaluate the acidic character of the surface of the activated carbons according to Boehm's procedure [26]. The amounts of various acidic oxygen functional groups (carboxyls, lactones, phenols and carbonyls) were measured by selective neutralization using bases of different strength. Approximately 0.5 g of each sample was mixed with 50 ml of a 0.1 N solution of a base (NaOH, Na₂CO₃, NaHCO₃, NaOC₂O₅). The suspension was shaken for 24 h at room temperature. After that time, the solution was filtered and an aliquot was taken. The amount of each base neutralized by the activated carbon was determined by back-titration using HCl 0.1 N solution.

The nitrogen adsorption at –196 °C was carried out in a Micromeritics ASAP 2020 automatic adsorption apparatus. The samples were initially outgassed at 150 °C and up to a vacuum of 10^{–6} mm Hg. The volume of adsorbed nitrogen was measured from a relative pressure of 10^{–7} up to 0.995. The isotherms were analyzed using different methods such as the BET method [27] for determination of surface area, the BJH method [28] for determining the volume of mesopores and t-plot for determining the volume of micropores [29]. The total pore volume was taken from the measurement of adsorbed nitrogen at a relative pressure of 0.995.

2.3. Toluene adsorption

The adsorption–desorption isotherms of toluene were determined gravimetrically using an automatic adsorption apparatus (VTI Co). The temperature of the sample, 25 °C, was monitored during the experiment and a pressure transducer monitored the pressure of the system. For each experiment 80 mg of activated carbon was taken. Initially the sample was outgassed at 150 °C and up to a vacuum of 10^{–6} mm Hg. After cooling to 25 °C toluene was introduced in the system to obtain the adsorption and desorption isotherms.

3. Results and discussion

3.1. Characterization of samples

Elemental analysis and yield of activated carbons (calculated as 100 × mass of AC / mass precursor) are included in Table 2. Activated carbons show a low content in nitrogen and a negligible amount of sulfur. Activated carbons prepared under oxidant atmosphere and at lower activation temperatures (400 °C) show a higher amount of oxygen [12].

Activated carbons prepared at low and intermediate impregnation ratio show higher yields [30,31]. It can be attributed to the decomposition of the polymeric structures of the activated carbons during the activation stage that release most elements different from carbon (N, H and O). Activating agent employed permits the dehydration, depolymerization and the redistribution of the constituent polymers, and the conversion of aliphatic groups to aromatics, increasing

Table 1

Preparation conditions of the activated carbons and labeling of samples.

Sample	Temperature (°C)	IR ^a	Time (min)	Atmosphere
AT400R1t75	400	1	75	N ₂
AT400R15t30	400	1.5	30	N ₂
AT467R117T45	467	1.17	45	N ₂
AT533R083t60	533	0.83	60	N ₂
AT600R1t30	600	1	30	N ₂
AT400R1t75-ox	400	1	75	8% O ₂ /N ₂
AT400R15t30-ox	400	1.5	30	8% O ₂ /N ₂
AT467R117T45-ox	467	1.17	45	8% O ₂ /N ₂
AT533R083t60-ox	533	0.83	60	8% O ₂ /N ₂
AT600R1t30-ox	600	1	30	8% O ₂ /N ₂

^a Impregnation ratio: amount phosphoric acid (g)/amount almond shell (g).

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