



Adsorption of SO₂ onto waste cork powder-derived activated carbons

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HIGHLIGHTS

- ▶ Activated carbon was successfully prepared from waste cork powder.
- ▶ Chemical and physical activation successfully developed carbon porosity and surface acidity.
- ▶ Chemically activated carbon presented the highest SO₂ adsorption capacity.
- ▶ SO₂ adsorption strength increased in more basic carbon surfaces.

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ABSTRACT

Three activated carbon samples have been prepared by thermal (AC_{char}), physical (with CO₂, AC_{CO2}) and chemical (with KOH, AC_{KOH}) activation of waste cork powder. Cork was characterized by thermogravimetric, elemental and proximate analyses, and activated carbons were characterized by elemental and proximate analyses, adsorption–desorption of N₂, acid/base and Boehm's titration and FTIR (ATR) spectroscopy. A commercial activated carbon sample (AC_{com}) was subjected to the same characterization program for comparison purposes. Activation of cork conducted to an increase in BET surface area and pore volume in the sequence: AC_{char} < AC_{CO2} < AC_{KOH}, getting close to those of AC_{com}, and to an increase in surface acidity in the sequence: AC_{char} < AC_{CO2} ≈ AC_{com} < AC_{KOH}. The four adsorbents were tested in the adsorption of SO₂, where AC_{KOH} presented the highest adsorption capacity, while AC_{char} and AC_{CO2} presented similar behaviors, comparable to that of AC_{com}. Adsorption equilibrium was successfully fitted to Langmuir and Freundlich isotherms. Desorption experiments demonstrated how SO₂ strong adsorption was favored when decreasing surface acidity.

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1. Introduction

Atmospheric pollution stands as one of the most important environmental issues, conducting to great social impact problems, such as acid rain, depletion of the ozone layer, photochemical smog or *greenhouse* effect. Among the atmospheric pollutants, SO₂ is a critical one, being a major responsible for acid rain, in addition to its inherent toxicity. SO₂ is released in a number of industrial activities, such as combustion processes, refining of sulfur-rich minerals or production of sulfuric acid. The most extended technologies for the removal of this pollutant are based on solid–gas reactions over inorganic solids, such as dolomites or calcium oxide, or on gas–liquid processes, using alkaline materials, like lime slurry or ammonia [1,2]. Adsorption on activated carbon appears as a promising and cheaper technology, which can, in turn, remove simultaneously nitrogen oxides [3]. The removal of SO₂ employing activated

carbon has been reported for commercial [4–10] and fossil-derived laboratory [5,7,8,11–14] samples, however, little work has been done concerning waste materials. It is worth flagging the work of Molina-Sabio et al. who reported the adsorption of CO₂ and SO₂ over apricot stone derived microporous carbons [15], Yavuz et al., in turn, employed olive industry residues for SO₂ removal [16], while Bashkova et al. used sewage sludge as carbon source [17].

Cork powder is the main residue of cork industry, being generated throughout all the fabrication stages of cork products (milling, sanding, cutting, etc.), and representing 25–30% of the raw material. Portugal is the major cork manufacturer, followed by Spain, summing up more than 70% of the cork powder generated worldwide. This residue has been traditionally employed as combustion fuel and to a lesser extent, as agricultural substrate or as a source of chemicals [18]. Recently, cork powder has attracted attention as a raw material for the preparation of activated carbons, where both chemical [19–22] and physical [22] activation have conducted to microporous materials with good adsorption performance in both the liquid and the gas phases.

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According to the exposed above, herewith we report the preparation and characterization of activated carbon from cork powder under different activation conditions, and explore its use as SO_2 adsorbent. Detailed characterization, as well as equilibrium and desorption data are provided, demonstrating the valorization of a waste material that even outperforms a commercial activated carbon sample.

2. Experimental

2.1. Activated carbon preparation and characterization

Cork powder (fraction < 0.17 mm) was supplied by Sanvicork S.A. (Extremadura, Spain), and subjected to thermogravimetric analysis; in order to study the transformations occurred upon thermal treatment. With that purpose, ca. 10 mg of cork powder were placed in a SDT Q600 unit (TA Instruments) and ramped from room temperature to 750 °C at 15 °C min^{-1} in a flow of N_2 (100 $\text{cm}^3 \text{min}^{-1}$). Weight loss was continuously monitored to better than 0.1 μg and acquired/manipulated using the TA Instrument Explorer software.

Carbonization of the raw material, i.e. bare thermal activation was conducted in a ceramic tube (10 cm i.d.) located in a horizontal furnace (ENERGON HLT 18-50-14) electrically heated. Typically, 1 g of cork powder filled a ceramic capsule located in the tube and was heated from room temperature to 750 °C at 5 °C min^{-1} in a flow of N_2 (100 $\text{cm}^3 \text{min}^{-1}$, mass flow controlled) with no further maintenance at that temperature, and allowed to return to room temperature under the same flow, in order to preserve the carbon from oxidation. Physical activation was conducted in two steps; first, cork powder was carbonized as above, and when the sample reached 750 °C, N_2 was switched to CO_2 , keeping these conditions for 2 h, with subsequent return to room temperature, as described above. Chemical activation employed KOH as activating agent. Typically, cork powder (ca. 25 g) was mixed with KOH (1:1 w/w), diluted in deionized water (5 cm^3 per gram of KOH), continuously stirred at 85 °C for 4 h and dried overnight at 110 °C in static air. The resulting material was subjected to carbonization in N_2 as described above, washed with HCl (1 M) to remove the activating agent and further washed with deionized water until the wash water approached neutral pH. At this point, three carbon samples have been obtained from cork powder, i.e. *via* bare thermal treatment (AC_{char}), *via* physical activation (AC_{CO_2}) and *via* chemical activation (AC_{KOH}). A commercial activated carbon sample (Panreac) was used for comparison purposes (AC_{com}).

Surface area/porosity measurements were conducted using a Quantasorb Sorption System (Quantachrome Instruments) with N_2 (at -196 °C) as sorbate. Prior to analysis, the samples were out-gassed overnight at 180 °C. Total specific surface areas were determined by the multipoint BET method at $P/P_0 \leq 0.3$, total specific pore volumes were evaluated from N_2 uptake at $P/P_0 = 0.99$ and total specific micropore volumes were determined using the standard Dubinin–Radushkevich treatment. Average micropore widths were calculated according to Dubinin–Stoeckli equation. Acid/base titrations were performed by immersing 25 mg of carbon in a 50 cm^3 solution of NaCl (0.1 M), basified with 0.5 cm^3 of NaOH (0.1 M) with constant stirring under inert atmosphere. To facilitate carbon dispersion, the solution was sonicated for 15 min. A 0.1 M HCl solution was used as titrant, added dropwise and the pH was monitored using a Crison GLP21 pH-meter. The starting NaCl (plus NaOH) solution served as a blank. Boehm titrations were conducted by immersing four 0.25 g fractions of carbon in 50 cm^3 0.05 M solutions of NaOH, Na_2CO_3 , NaHCO_3 and HCl, respectively, under continuous stirring for 24 h. Next, the solutions were filtered, and 5 cm^3 of the liquids filtered were titrated either

with HCl (0.1 M) or NaOH (0.1 M) to evaluate the base or acid excess, respectively [23]. The carbon, hydrogen, nitrogen and sulfur (CHNS) content of the carbon materials under study, as well as of the starting cork powder was determined using a LECO CHNS-932 unit. The carbon (ca. 2 mg) combustion (at 1000 °C) products were analyzed by IR (for C, H and S content) and TCD (for N content). Proximate analysis was conducted in order to determine moisture, volatile matter, fixed carbon and ash in the raw cork and the carbons studied, under ASTM specified conditions. These experiments were carried out in the thermogravimetric unit described above, according to the following steps (TA Instrument Technical Note-129); (a) 10 mg of sample were ramped from room temperature to 200 °C at 25 °C min^{-1} under a flow of N_2 (60 $\text{cm}^3 \text{min}^{-1}$), (b) 5 min isothermal hold, (c) ramp to 900 °C at 50 °C min^{-1} , (d) 10 min isothermal hold, (e) switch gas to O_2 (60 $\text{cm}^3 \text{min}^{-1}$), and (f) 15 min isothermal hold. The FTIR spectra of the carbon samples were obtained using a Perkin–Elmer Spectrum GX spectrometer with an Attenuated Total Reflectance (ATR) attachment with a ZnSe crystal. Before the spectrum of a sample was recorded the background line obtained was automatically subtracted. The spectra were recorded from 2000 to 650 cm^{-1} at a scan rate of 0.2 cm s^{-1} , and the number of interferograms with a nominal resolution of 4 cm^{-1} was fixed at 16.

2.2. Adsorption of SO_2

Adsorption experiments were conducted in the thermogravimetric analyzer described above, at 45 °C. In each experiment, a flow of SO_2/N_2 contacted the sample. Carbon samples were sieved into a batch of 75 μm . The total flow was kept constant at 120 $\text{cm}^3 \text{min}^{-1}$, while the SO_2 concentration spanned the range 500–10,000 ppm, and the weight gain was continuously monitored by the analyzer. In order to evaluate the adsorption strength, desorption experiments were done. A previous adsorption (2500 ppm_{SO_2}) was conducted, followed by an isothermal hold in N_2 at 45 °C.

3. Results and discussion

3.1. Activated carbon preparation and characterization

Cork is a natural polymer with varying composition. Pereira et al. reported an average chemical composition of reproduction cork grown in Portugal and averaged to four growing sites and 10 trees per site. A summative chemical analysis revealed a composition of ca. 1, 14, 40, 23 and 20% w/w corresponding, respectively, to ashes, extractives, suberin, lignin and polysaccharides [24]. Additionally, our supplier company confirmed the presence of other chemicals involved in the manufacturing process, i.e. sulphamic acid from the whitening treatment, H_2O_2 and NaOH from subsequent washing and glue (polyurethane) from clogging. On this basis, in order to arrive at a suitable temperature for the carbonization of the raw matter, the cork powder was subjected to thermogravimetric analysis in N_2 , as shown in Fig. 1. A first mass decay occurs in the temperature range 20–130 °C ($T_{\text{max}} \approx 40$ °C), corresponding to ca. 2% of the initial mass. Comparable mass losses have been reported in the literature, both in N_2 [25] and air [26] atmospheres, attributable to the evaporation of water adsorbed on the sample. A second mass decay, ranging from ca. 200 to >500 °C involves different events and needs a detailed study. A first event, in the temperature range 200–330 °C ($T_{\text{max}} \approx 310$ °C) can be attributed to the decomposition of hemicellulose, as reported by Yang et al. who studied the decomposition of lignin, cellulose and hemicellulose under comparable experimental conditions [27]. A second event, appearing as a wide shoulder between 315

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