



Tailoring activated carbons for the development of specific adsorbents of gasoline vapors



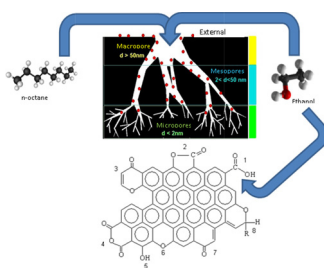
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HIGHLIGHTS

- High performance adsorbents of gasoline vapors as have been developed.
- The influence of their surface chemistry and porosity was determined.
- Ethanol adsorption is favored by specific interactions with carboxylic groups.
- VOC' diffusion is favored by mesopores and the adsorption capacity by micropores.
- The VOC' adsorbed is totally recovered by thermal regeneration.

GRAPHICAL ABSTRACT



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ABSTRACT

The specific adsorption of oxygenated and aliphatic gasoline components onto activated carbons (ACs) was studied under static and dynamic conditions. Ethanol and n-octane were selected as target molecules. A highly porous activated carbon (CA) was prepared by means of two processes: carbonization and chemical activation of olive stone residues. Different types of oxygenated groups, identified and quantified by TPD and XPS, were generated on the CA surface using an oxidation treatment with ammonium peroxydisulfate and then selectively removed by thermal treatments, as confirmed by TPD results. Chemical and porous transformations were carefully analyzed throughout these processes and related to their VOC removal performance. The analysis of the adsorption process under static conditions and the thermal desorption of VOCs enabled us to determine the total adsorption capacity and regeneration possibilities. Breakthrough curves obtained for the adsorption process carried out under dynamic conditions provided information about the mass transfer zone in each adsorption bed. While n-octane adsorption is mainly determined by the porosity of activated carbons, ethanol adsorption is related to their surface chemistry, and in particular is enhanced by the presence of carboxylic acid groups.

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1. Introduction

The control of volatile organic compound (VOC) emissions is today one of the most difficult environmental challenges. VOC emissions are produced in many different industrial or domestic

processes causing serious damage to health, materials and the environment. Both destructive (oxidation) and recovery (adsorption, condensation) techniques are described in the bibliography [1–5] depending on the source of the VOC and its concentration. Emissions associated with the use of fuels in vehicles are of particular importance and there is a clear need to develop effective technologies and strategies to improve the quality of the air we breathe. A lot of research has been done for example on improvements to tailpipes for exhaust gas decontamination [6,7]. Wang et al. [8]

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identified a total of 57 individual VOCs in the exhaust gas of gasoline vehicles.

Historically, less attention has been paid to evaporative emissions produced during fuel storage and/or transfer. Nevertheless, a number of papers have been published also on this topic [9,10]. For example, Yamada quantified evaporative emissions as the sixth highest source of VOC in Japan, with 4.6% of total VOC emissions [9]. Specific devices (canisters) for adsorbing VOCs have been developed, which mainly use activated carbons as the adsorbent [11–13]. Furthermore, the American Petroleum Institute (API) has continuously pointed out the effects of these vapors on the environment, health and safety [14], analyzing tank and pipeline regulations to ensure the safe transport, storage and disposal of gasoline.

In recent years there has also been increasing interest in ethanol-based fuels all over the world. The addition of ethanol to gasoline is interesting from an environmental and economic point of view since it can be produced from biomass. Moreover, ethanol is added to gasoline as an anti-knock agent because it is less harmful than MTBE and ETBE. However, the presence of ethanol in fuels is the subject of controversy, since some studies have proved that ethanol-based fuels produce larger quantities of evaporative emissions [15,16].

Some empirical models have been developed in order to estimate evaporative emissions from canister-equipped vehicles [9–12]. These models considered several factors such as vehicle design (tanks), ambient temperature, driving conditions, or gasoline volatility [13] but there is a lack of experimental confirmation of the relationship between canister performance, gasoline composition and the characteristics of the adsorbent, as indicated by Yamada [9]. Activated carbons (ACs) are the most widely used adsorbent due to the fact that both their porous and chemical nature can be easily tailored. Moreover, cheap ACs can be produced from raw materials such as agricultural residues [2,5,17,18]. In comparison, zeolites are about ten times more expensive [19].

In this work, we prepared a series of ACs from olive stones. We developed the porous texture by chemical activation and modified the surface chemistry by means of a severe oxidation process. After that, a selective removal of oxygenated surface groups was performed in order to find out more about specific VOC-AC interactions, which may affect the adsorption and regeneration capacities. Ethanol and n-octane were selected as target VOCs because they are the main components of gasoline and have different chemical natures (ethanol is hydrophilic and n-octane is hydrophobic). Finally we correlated the evolution of porosity and chemical surface characteristics for these activated carbons with their ethanol and n-octane adsorption performance under static and dynamic conditions.

2. Materials and methods

2.1. Activated carbon synthesis by KOH activation

Olive stones were milled and sieved to 1.0–2.0 mm, treated with sulfuric acid (1 N) in order to remove any remains of the pulp and then washed until all sulfates had been removed. A two-stage activation procedure was designed: initially, olive stones were carbonized at 400 °C for 2 h under a nitrogen flow (300 cm³ min⁻¹) and then the char obtained was chemically activated using a mixture of char and KOH in a 1:7 mass ratio. This mixture was treated under nitrogen flow (300 cm³ min⁻¹) for 2 h at 350 °C followed by 3 h at 850 °C (heating rate 10 °C min⁻¹). The sample was kept under nitrogen atmosphere while it was cooled to room temperature. Finally, it was treated with HCl and HF, which also removed the excess base (KOH), washed with distilled water till all chlorides had been

removed and dried in an oven at 110 °C for 24 h before storage. This sample was called CA.

2.2. Chemical surface modifications

Ammonium peroxydisulfate ((NH₄)₂S₂O₈) was chosen as the oxidizing agent [20]. CA was mixed with a saturated solution of this salt on H₂SO₄ 1 M. After 24 h under stirring at room temperature, oxidized carbon was filtered and washed with distilled water several times until all sulfates had been removed. This material was dried at 110 °C and labeled as CAOX. Thermal treatments under nitrogen atmosphere (150 cm³ min⁻¹) at 300 °C, 500 °C and 700 °C (10 min, 20 °C min⁻¹) were carried out on different portions of CAOX in order to selectively remove oxygenated surface groups (OSG). These samples were labeled as CAOX300, CAOX500 and CAOX700.

2.3. Textural characterization

The corresponding N₂ and CO₂ adsorption isotherms at –196 °C and 0 °C were obtained using an AUTOSORB 1 (QUANTACHROME Ins.) instrument. Parameters such as BET surface area, micropore volume (*W*₀) and micropore mean width (*L*₀) were calculated by applying BET, Dubinin–Radushkevich and Stoeckli equations to isotherms [21,22]. Pore size distribution (PSD) curves were obtained by DFT or BJH derived methods [23,24]. Mesopore volume (*V*_{meso}) was estimated considering the total pore volume as the volume of nitrogen adsorbed at a relative pressure *P*/*P*₀ = 0.95 (*V*_{0.95}). Therefore, *V*_{meso} was obtained from the difference between *V*_{0.95} and *W*₀ (N₂). Mercury pycnometry was carried out in order to determine the apparent density of samples. In preparation for this procedure, samples were previously degasified at 110 °C under dynamic vacuum (10⁻³ Torr).

2.4. Chemical characterization

Thermal Programmed Desorption (TPD) curves of carbon monoxide and carbon dioxide were recorded. The analysis of TPD profiles enabled us to quantitatively determine the total oxygen content and the number of different oxygenated groups. The assignment of these groups was based on the bibliography [25–28]. Experiments were carried out by heating around 150 mg of sample at 50 K min⁻¹ up to 1273 K using He as the carrier gas (60 cm³ min⁻¹). The analysis of desorbed gases was performed with a Mass Spectrometer model Prisma (Pfeiffer).

X-ray photo emission spectra (XPS) were recorded using a Kratos Axis Ultra-DLD spectrometer. As a radiation source this instrument uses MgKα (*hν* = 1253.6 eV) and a hemispheric electron analyzer operating at 12 kV and 10 mA. Since we wanted to quantify total oxygen content, we analyzed regions for C_{1s} and O_{1s}. The deconvolution of spectra and the assignment of bands were also performed according to the bibliography [28,29].

Zero-point charge pH (pH_{ZPC}) of samples was determined with the method proposed by Leon et al. [30]. Approximately 250 mg of each sample were suspended on 4 mL of distilled water previously degasified. Suspensions were stirred and thermostated at 25 °C measuring the pH periodically until readings were constant. The final pH obtained this way was considered as the pH_{ZPC} for each sample.

2.5. VOC adsorption

2.5.1. Static adsorption

Ethanol and n-octane static adsorption experiments were carried out by exposing 0.050 g of each sample, previously dried at 110 °C, in a desiccator containing ethanol (absolute ethanol,

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