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# Activated carbon monoliths from particle stabilized foams

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ABSTRACT

Particle stabilized liquid foams are used as templates to obtain carbon-based porous materials with open cell structure, high specific area and hierarchical porosity. This route relies on gel casting to strengthen the structure of the liquid foams, followed by high temperature treatment to eliminate organic components and obtain solid foams.

The liquid foam stabilizer was a commercial activated carbon powder, characterized by high porosity and irregular morphology of the particles, associated with a cationic surfactant. The micro-structure and the textural properties of the final solid materials have been investigated by Scanning Electronic Microscopy and Nitrogen adsorption methods. The results show that this method can be used to fabricate high specific area porous materials in the form of monoliths, with adequate consistence and mechanical resistance. The materials obtained seem promising for many practical applications such as gas adsorption, filtering and catalysis.

## 1. Introduction

Solid particles dispersed in aqueous media, depending on their composition, surface charge, morphology and size, have been widely employed as stabilizers of foams and emulsions. In many applications micro-nanosized particles are associated to appropriate surfactants in order to obtain the correct degree of hydrophobicity to favor their transfer to the liquid interfaces or the incorporation in the adsorbed layer [1–6].

Particle stabilized emulsions and foams have been increasingly attracting the attention of the scientific community because of their unique properties related to the control of stability and morphology, or drop/bubble size distribution. Such properties make them potentially applicable in a huge number of research and technological fields, among them the fabrication of porous materials with tailored structure, where wet foams and emulsions are used as templates [7–14].

Solid foams with specific open cell structure, at high specific area and hierarchical porosity, are appealing materials for many practical applications such as gas adsorption, filtering and catalysis and this is even more true if carbon based materials are concerned [15–20].

Carbon is, in fact, a widely exploited material in many industrial and technological applications because of its characteristics of chemical inertness, electrical conductivity and thermal stability. For example, relevant non-crystalline carbon materials have been recently studied for energy applications [21,22]. Moreover, in the form of Activated Carbon (AC), the high degree of porosity makes it appropriate for gas adsorption, waste treatment, chemical recovery operations or industrial purification [23–27].

Among the novel routes to produce carbon based porous materials, which are continuously under development, those relying on the solidification of particle-stabilized liquid foams, mainly developed for the synthesis of different kind of ceramic materials [12,28] have been applied in an increasing number of cases also for carbon based porous materials [29].

In previous works [29–31] we proposed a method where liquid foams stabilized by carbon colloidal particles were used as template for a gel-casting process. The "green bodies" so obtained were then treated at high temperature to eliminate the organic components and obtain porous carbon materials with interesting hierarchical porosity.

From the analysis of the samples obtained by this method, it was pointed out that the structure of the final solid foams was significantly dependent on the properties of the precursor liquid foams which, in turns, depend on the composition of the initial dispersion.

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A key aspect of this method is, in fact, the association of adequate surfactant components to the colloidal particles to favor their transfer to the water/air interfaces and stabilize the liquid foam [30]. For this reason, the formulation of the initial dispersion requires parallel investigations on their interfacial and bulk properties to monitor and select the right degree of the particle amphiphilicity.

Compared to other direct foaming routes based on the association of gel-casting and thermal treatments reported by other authors [12,28], the peculiarity of our approach is the utilization of the physicochemical analysis of the initial dispersions as a fundamental step to establish the structural and mechanical properties of the final materials.

In this work, we obtain highly porous carbon materials using, as foam stabilizer, a commercial AC powder associated to a cationic surfactant.

AC is the best known example of porous carbon [32–36] which may derive from chars, carbonized natural products/vastes (wood, fruit shells and stones, lignite, etc.), highly volatile bituminous coals [37], partially gasified with stream or carbon dioxide, to increase their porosity [38,39]. Due to their origin, low cost and large availability in several region of the world, AC is largely used in many practical applications as gas adsorbent material.

As shown in details in the following, the utilization of an AC powder, characterized by highly poly-dispersed size distribution of the particles, which also has high porosity and irregular morphology, allows obtaining solid foams with very high specific area (comparable with those of the initial AC powder) in a form of monoliths, with fair consistence and mechanical resistance, very promising for the development of gas adsorption devices.

Compared to other well consolidated techniques such as those based on pyrolysis [40] and high pressure treatments [23,41,42], our protocol allows producing highly porous carbon monoliths by a very simple procedure that utilizes “low cost” and green components.

## 2. Materials and methods

### 2.1. Materials

The Activated Carbon used in this work was a charcoal powder purchased by VWR (Activated Charcoal VWR) and used as received. As evidenced by the preliminary SEM images (Fig. 1a) the dry powder is composed by submicron particles with high variability in shape and average particle size around 130 nm, when dispersed in aqueous media (Fig. 1b).

The cationic surfactant, hexadecyltrimethylammonium-bromide (CTAB) as well as the components used to induce gel-casting in foams, i.e. Polyvinyl alcohol (PVA), the cross-linker 2,5-dimethoxy-2,5-dihydrofuran (DHF) and Nitric acid (HNO3), were supplied by Sigma-Aldrich (Germany) and used as received.

Water used for dispersions was obtained by a multi-cartridge system (Millipore, Elix plus Milli-Q), providing a resistivity greater than 18 MΩ cm and surface tension of 72.5 mN/m without any appreciable kinetics over several hours.

### 2.2. Analysis of the dispersion

#### 2.2.1. Dynamic light scattering and ξ-potential

Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano (Malvern Instruments, UK), in order to evaluate the size distribution of the carbon particles in the aqueous dispersions against the surfactant concentration. The intensity correlation function is obtained using the red line ($\lambda = 632$ nm) of a He–Ne in a quasi-backscattering configuration ($\theta = 173°$). The analysis of the normalized second order correlation functions $g^2(t)$ by a standard inverse Laplace algorithms, provides the apparent diffusion coefficient and, through the Stokes-Einstein relation, the particle hydrodynamic diameter [43].

In order to estimate how the surface charge of particles in the dispersion is modified by the interaction with the ionic surfactant molecules, ξ-potential measurements were also performed as a function of the surfactant concentration, by the same Malvern instrument. The concerned technique is based on the electrophoretic mobility measurement according to the laser Dopler electrophoretic method [44].

All measurements were performed in disposable standard cells at controlled temperature of 25 °C.

#### 2.2.2. Surface tension measurements

The surface tension of surfactant solutions and dispersions was measured by a Profile Analysis Tensiometer [45] (PAT-1 by Sinterface, Germany). based on the acquisition of the gravity deformed profile of a pendant drop under mechanical equilibrium. The surface tension is obtained fitting the theoretical profile calculated through the Laplace Equation to each experimentally acquired drop profile. More details on this technique are reported in Ref. [45]. For the present study a drop is formed at the tip of a Teflon capillary tube and the surface tension acquired during the equilibration of the adsorption layer, while the drop surface area is maintained at a constant value, typically, of 30 $mm^2$.

### 2.3. Fabrication of the porous materials

#### 2.3.1. Preparation of dispersions, liquid foams and green bodies

Mixed surfactant-particle dispersions are prepared in an ultrasound bath, adding drop by drop the CTAB solution to a given amount of AC powder dispersed in pure water. In this way dispersions at different compositions are obtained corresponding to different particle/surfactant concentration ratio. These dispersions are used for investigating the role of surfactant in modifying the surface charge of the AC particles determining their degree of amphiphilicity.

The processing route presented in this work relies on gel casting to strengthening the structure of liquid foams which are used as templates to produce porous materials.

To this aim, an aqueous solution of PVA at concentration of 7.8 wt %, is added to the particle dispersion previously prepared and then maintained under stirring for a time of about 12 h. The volume of the PVA solution added was equal to that of the particle dispersions so that, for all the samples investigated, the PVA concentration in the precursor was 3.9 wt%.

To activate the gelling process, 10 min before foaming, nitric acid is incorporated into the dispersion, still under stirring, and just before foaming a cross-linking agent, DHF, is also added.

Foams are then produced by aerating this mixed surfactant-particles-polymer dispersions using a mixer IKA ULTRA TERPAX T25, at 8000 rpm for about 2 min.

Immediately after their generation, the foams are transferred to the oven and left for 3–4 h at temperature of 80 °C, until gel-casting is completed. In this way, the in situ solidification of the polymer dissolved in the liquid foam matrix blocks the structure of the freshly generated foams. The obtained bodies are left for cooling, at room temperature, then are removed from beakers and dried in the air for at least 2 days.

These porous samples are called here and in the following “green body” which, in analogy with the terminology related to ceramic processing, refers to the dry solid samples ready for high temperature treatment or sintering.