

CO₂ CAPTURE ON ACTIVATED CARBONS UNDER REALISTIC OPERATION CONDITIONS

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Introduction

Anthropogenic CO₂ emissions induce global warming due to greenhouse effect. With concentration reaching values higher than 405 ppm in September 2018, the CO₂ concentration is moving closer to the 450 ppm critical value [1]. In order to reduce CO₂ emissions, adsorption processes (PSA, VPA...) can be used on CO₂ emission sites. Such processes require porous materials for the adsorption step. Activated carbons (ACs) have high specific areas and microporous volumes, high CO₂ adsorption capacities at low temperature, and high thermal and chemical stability that make them suitable candidates for CO₂ capture [2]. In the present study, the CO₂ capture performances of ACs derived from phenolic oil were evaluated under realistic conditions. The direct valorization of phenolic oil using a sol-gel process followed by an activation step is an interesting means of valorizing such byproduct of brown-coal pyrolysis. The assessment of ACs textural properties allows a good understanding of CO₂ adsorption phenomenon. The evaluation of CO₂ capture efficiency under realistic conditions put into perspective the potential use of the ACs in operational systems.

Materials and Methods

The gelation of phenolic oil (PO) was carried out in isopropanol (iP), n-propanol (P) or water (W), using formaldehyde as crosslinker. After solvent exchange, using ethanol or isopropanol, the materials were dried either by thermal convection (ethanol, 85°C, 12h) or by lyophilization (tert-butanol, 35°C, 3 days). The dried gels, recovered after the classical convective drying, were named xerogels (X) while those recovered after lyophilization were named cryogels (C). Finally, 3 sets of dried gels were recovered: XiPPO, XPPO and CWPO. p-toluenesulfonic acid was used in the synthesis of the XiPPO series, while catalysis in alkaline medium (NaOH) was used in the synthesis of XPPO and CWPO materials. The dried gels were then activated at 750°C (N₂, 100 mL min⁻¹) using potassium hydroxide (KOH). The KOH/dried gel mass ratios were set from 1 to 5. The activated carbons (ACs) were washed with 1 mol L⁻¹ HCl, and then with bi-distilled water in a Soxhlet for 5 days. The ACs were labeled by adding the KOH/gel mass ratio (i.e. 1, 2, 3, 4 or 5) to the name of the gel precursor. The textural properties (i.e., specific surface areas, pore size distributions) of the materials were determined using the non-local density functional theory (NLDFT) from the SAIEUS® routine and the combination of N₂ and CO₂ adsorption data (ASAP 2020, Micromeritics). The CO₂ capture capacities and isotherms were determined using a thermogravimetric analyzer (TA Q500) with a platinum pan that was filled with 8 mg of ACs. After a proper in-situ drying and degassing, the CO₂ adsorption (5-90 vol. % in N₂) was carried

out at several temperatures (i.e., in the 25-120°C temperature range). The performances of the synthesized ACs were compared with those of 2 commercial ACs (MSP-20X and MSC_30 from the KANSAI company).

Results and Discussion

Fig 1.a. shows the CO₂ adsorbed amount on the ACs under the most favorable conditions (90 vol. % CO₂ in N₂, 25°C). The synthesized ACs had similar, or better, CO₂ capture properties than those of commercial ones (i.e., 2.64 mmol/g for the MSP-20X and 2.86 mmol/g for the XPPO_1). In these conditions, the lower the average micropore size, L₀(dV), the higher the CO₂ capture efficiency. Due to pore widening during activation step, the pore size increased with the surface area. Therefore, the adsorbed amount decreased due to the lesser overlapping of adsorption potentials in these wider pores and to the unsaturated nature of the pores under these low CO₂ relative pressures P/P₀. This trend was confirmed by representing the specific adsorbed amount per unit of surface area as a function of the average micropore size (**Fig 1.b.**).

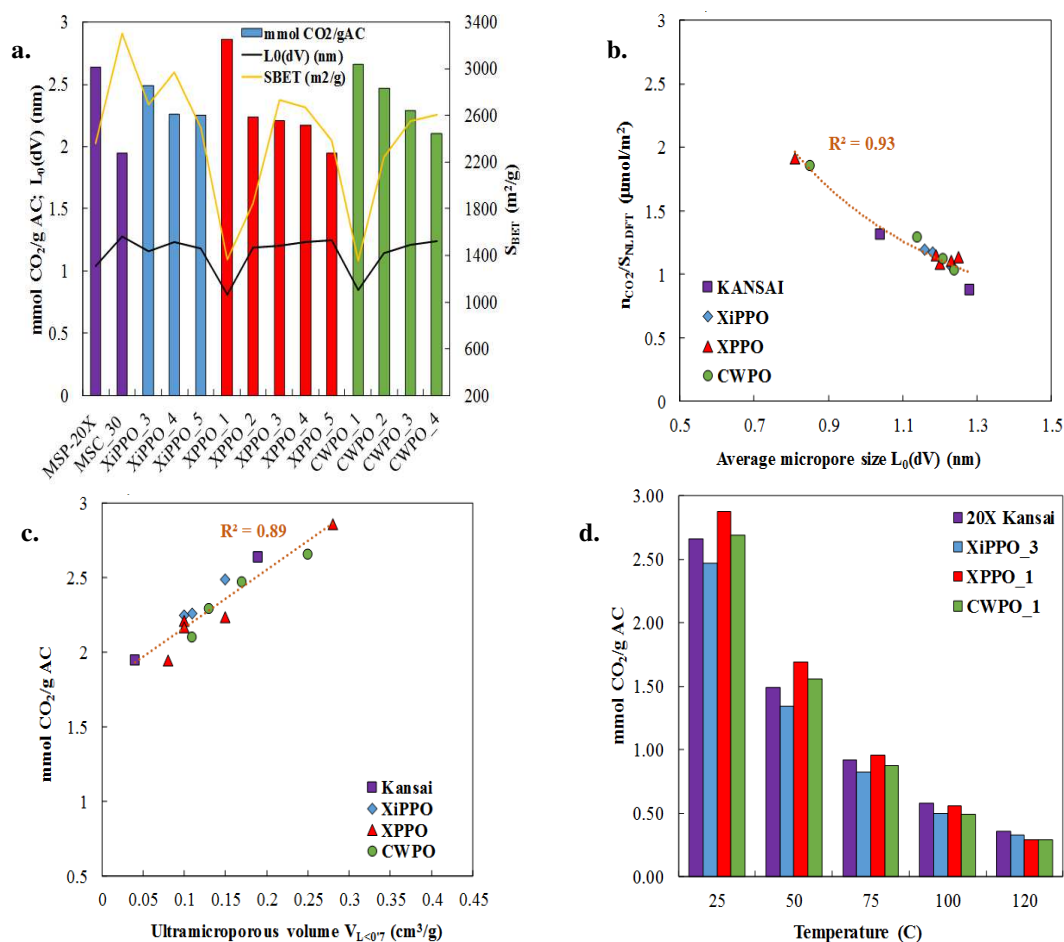


Figure 1. (a.) adsorbed amount of CO₂ (25°C, 90 vol. % CO₂ in N₂), average micropore size (L₀(dV), calculated from the pore size distributions) and BET area of the ACs, (b.) adsorbed amount per unit of surface area versus L₀(dV), (c.) adsorbed amount of CO₂ versus ultramicroporous volume and (d.) CO₂ capture efficiency of the best materials at several temperatures.

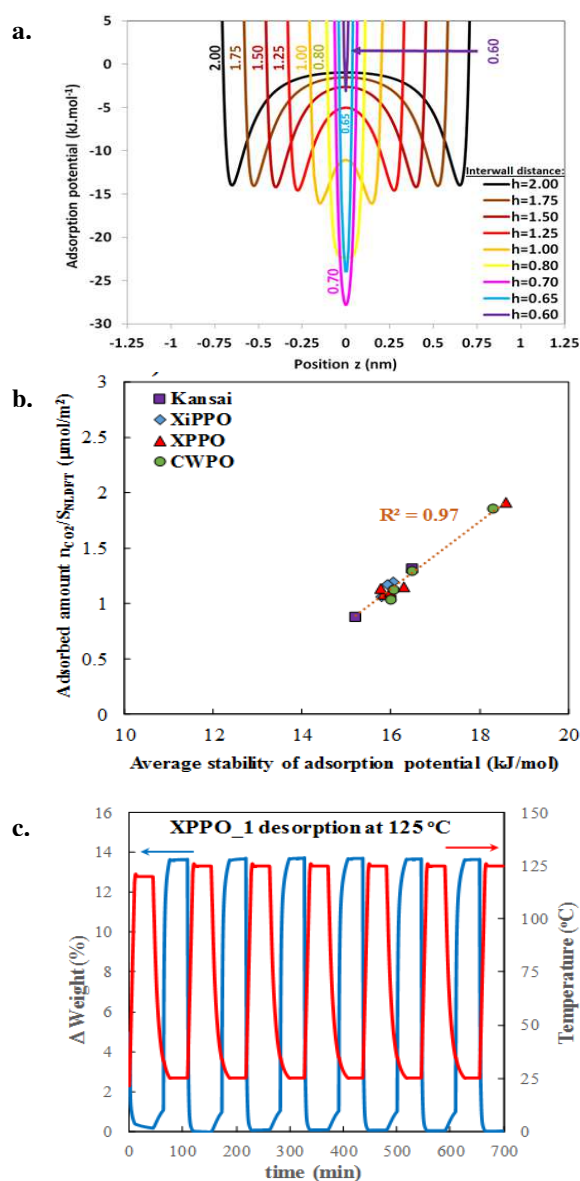


Figure 2. (a.) Steele's potential for several pore wall to pore wall distances (slit pore model for CO₂ in porous carbon), (b.) adsorbed amount per unit of surface area as a function of average stability of adsorption potential, and (c.) CO₂ adsorption/desorption cycles on XPPO_1 (25-125°C, 90-0 vol. % CO₂).

Furthermore, **Fig.1.c** confirmed the paramount importance of the ultramicropores ($L < 0.7$ nm) for CO₂ adsorption under these conditions. The CO₂ adsorbed amount indeed increased linearly with the ultramicroporous volume. **Fig.1.d** shows that the adsorbed amount followed an exponential-like decay depending on temperature and a progressive inversion between the samples when the temperature increased. For example, XiPPO_3 adsorbed less CO₂ than XPPO_1 at 25°C, but the situation was reversed at 120°C. At very low relative pressure (i.e., high temperature), the adsorption process is likely to become more sensitive to surface defects and chemistry than to the texture, explaining such inversion [3][4].

The small discrepancy exhibited in the trend of **Fig.1.b** can be reduced using a simple indicator accounting for the non-linearity of adsorption potential and, partly, for the difference of PSDs shape. The combined use of the PSDs and of the Steele's potential (**Fig 2.a.**) enables calculating the average stability of the adsorption potential for each material. At 25°C and 1 bar (90 vol. % CO₂ in N₂) the adsorbed amount per unit of surface area followed a linear trend with the average stability of adsorption potential (**Fig 2.b.**). This finding validates that the CO₂ adsorption only depends on textural properties under the conditions used in this study.

Finally, the adsorption/desorption cycles (90 vol. % CO₂ at 25°C switched to 100% vol. N₂ at 125°C) were carried out on the most promising material (XPPO_1) (**Fig.2.c**). Such adsorption/desorption cycling shows the perfect reversibility of CO₂ adsorption phenomenon and of the necessity of a good stability of the AC and mild temperatures for such regeneration.



Conclusion

This study showed that phenolic-oil is a suitable precursor of activated carbons (ACs). The as-synthesized ACs had, indeed, similar or better CO₂ adsorption properties than those of commercial ones. Under 25°C and 1 bar (90 vol. % CO₂ in N₂), the adsorbed amount of CO₂ depends on average micropore size and ultramicroporous volume. The use of the average stability of adsorption potential allowed evidencing this dependence on texture. At higher temperatures and very low CO₂ relative pressure, this dependence becomes less clear, and the surface chemistry and defects might play a more significant role. Finally, the CO₂ adsorption was perfectly reversible, and the stability of the ACs in operative conditions was clearly evidenced.

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