CO₂ CAPTURE ON ACTIVATED CARBONS UNDER REALISTIC OPERATION CONDITIONS

V. Fierro[1*], E. García-Díez[2], S. Schaefer[1], A. Sanchez-Sanchez[1],
M.M. Maroto-Valer[2], S. García[2], A. Celzard[1]

[1] Institut Jean Lamour, UMR 7198 CNRS and Université de Lorraine, Épinal, France
[2] Research Centre for Carbon Solutions (RCCS), School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom

*Presenting author e-mail: vanessa.fierro@univ-lorraine.fr

Introduction

Anthropogenic CO_2 emissions induce global warming due to greenhouse effect. With concentration reaching values higher than 405 ppm in September 2018, the CO_2 concentration is moving closer to the 450 ppm critical value [1]. In order to reduce CO_2 emissions, adsorption processes (PSA, VPA…) can be used on CO_2 emission sites. Such processes require porous materials for the adsorption step. Activated carbons (ACs) have high specific areas and microporous volumes, high CO_2 adsorption capacities at low temperature, and high thermal and chemical stability that make them suitable candidates for CO_2 capture [2]. In the present study, the CO_2 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 CO_2 adsorption phenomenon. The evaluation of CO_2 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 convectional drying, were named xerogels (**X**) while those recovered after lyophilization were named cryogels (**C**). Finally, 3 sets of dried gels were recovered: **X**iPPO, **X**PPO and **C**WPO. 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 (N_2, 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 N_2 and CO_2 adsorption data (ASAP 2020, Micromeritics). The CO_2 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 CO_2 adsorption (5-90

vol. % in N_2) 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 CO_2 adsorbed amount on the ACs under the most favorable conditions (90 vol. % CO_2 in N_2, 25°C). The synthesized ACs had similar, or better, CO_2 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, $L_0(dV)$, the higher the CO_2 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 CO_2 relative pressures P/P_0. 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.**).
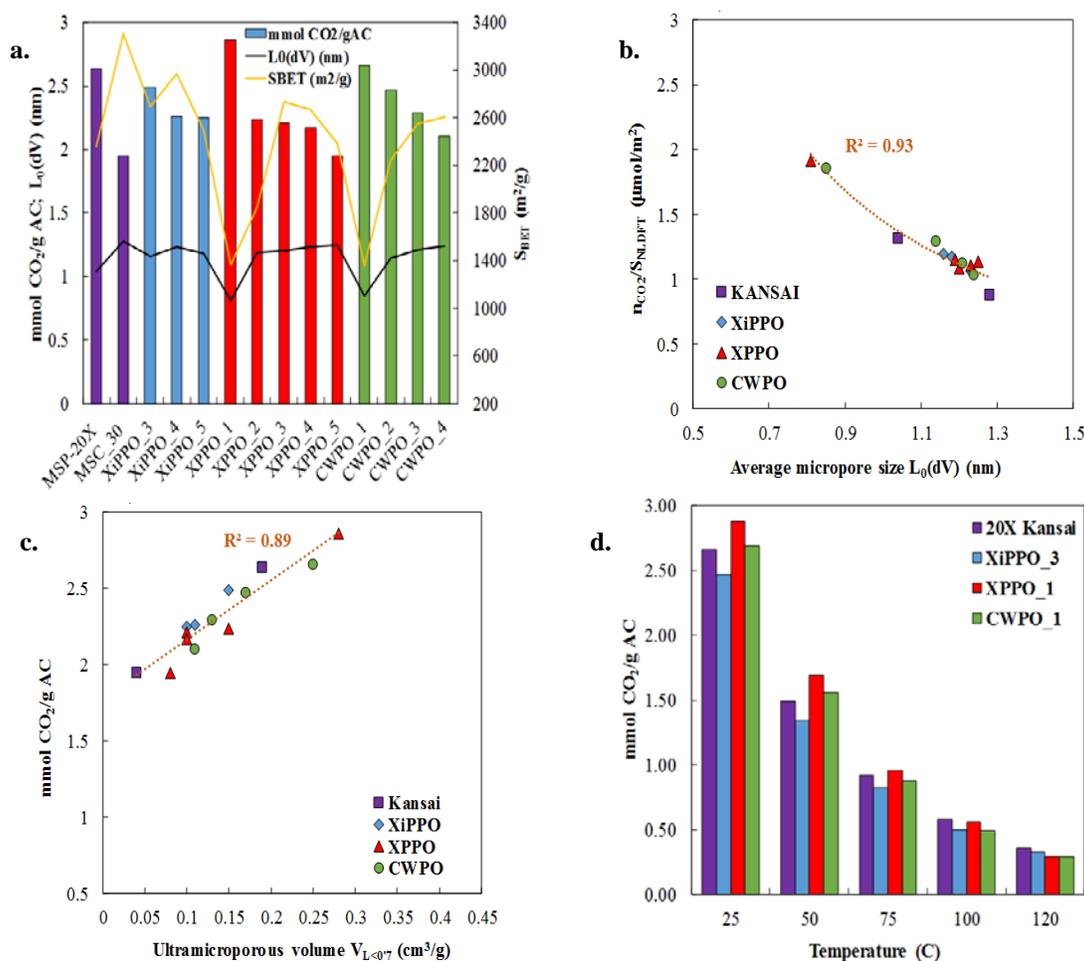

Figure 1. (**a.**) adsorbed amount of CO_2 (25°C, 90 vol. % CO_2 in N_2), average micropore size ($L_0(dV)$, calculated from the pore size distributions) and BET area of the ACs, (**b.**) adsorbed amount per unit of surface area versus $L_0(dV)$, (**c.**) adsorbed amount of CO_2 versus ultramicroporous volume and (**d.**) CO_2 capture efficiency of the best materials at several temperatures.
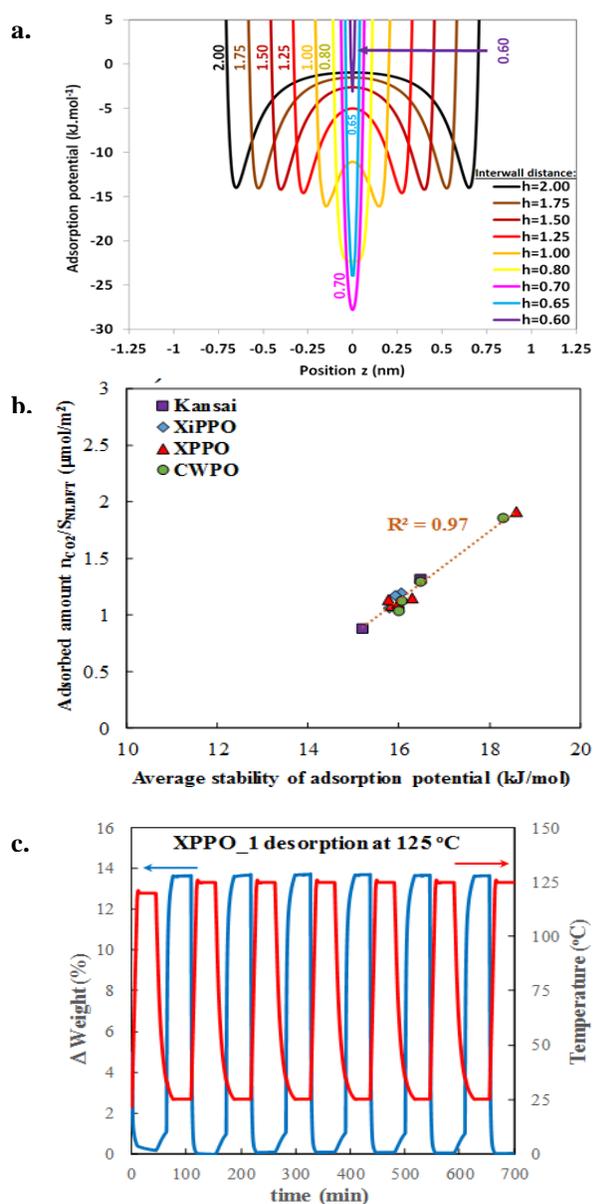
a.

b.

c.

Figure 2. (**a.**) Steele's potential for several pore wall to pore wall distances (slit pore model for CO_2 in porous carbon), (**b.**) adsorbed amount per unit of surface area as a function of average stability of adsorption potential, and (**c.**) CO_2 adsorption/desorption cycles on XPPO_1 (25-125°C, 90-0 vol. % CO_2).

Furthermore, **Fig.1.c** confirmed the paramount importance of the ultramicropores (L < 0.7 nm) for CO_2 adsorption under these conditions. The CO_2 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 CO_2 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 PDSs 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. % CO_2 in N_2) 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 CO_2 adsorption only depends on textural properties under the conditions used in this study.

Finally, the adsorption/desorption cycles (90 vol. % CO_2 at 25C° switched to 100% vol. N_2 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 CO_2 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 CO_2 adsorption properties than those of commercial ones. Under 25°C and 1 bar (90 vol. % CO_2 in N_2), the adsorbed amount of CO_2 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 CO_2 relative pressure, this dependence becomes less clear, and the surface chemistry and defects might play a more significant role. Finally, the CO_2 adsorption was perfectly reversible, and the stability of the ACs in operative conditions was clearly evidenced.

Acknowledgment

References

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