

TURNING TAR-DERIVED PHENOLIC OILS INTO POROUS CARBON GELS FOR WATER POLLUTANTS REMOVAL

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Introduction

Separation of coal tar into different fractions by distillation affords high-value products but also phenolic oils (POs). If phenol and cresols are the main reactive chemical species in POs, other chemicals such as coumarone and indene may also be found in large or significant amounts. On the other hand, coumarone-indene-phenol resins, and phenol- or cresol-derived gels are well-known materials. Thus, the driving idea of the present research was to propose an easy synthetic way of turning POs into high added-value carbon materials for water remediation. A one-pot synthesis in a monophasic organic medium was explored to produce solvogels. After drying the latter, the as-produced aero-, cryo- and xerogels were pyrolyzed to obtain the final carbon gels. Liquid phase adsorption assays of methylene blue (MB) were then carried out on one selected material. MB is indeed a commonly used molecule for such early stage of water pollutant removal studies.

Materials and Methods

15 g of PO and a variable amount of isopropanol (7.5, 10, 12.5, 15 or 17.5 g of solvent) were first mixed in a 50 mL beaker under vigorous stirring during 2 min. Then, 0.64 g of para-toluenesulfonic acid (PTSA) was solubilized under stirring (2-5 min) in the initial mixture. Next, 3.12 g of paraformaldehyde (crosslinker) were added and solubilized under stirring. The mixture was then poured in hermetically sealed sample tubes, which were subsequently placed in a previously heated (85°C) oven during 5 days. The solvogels were then extracted from the sample tubes and washed for 3 days with absolute ethanol. Finally, aerogels were produced using supercritical drying (CO₂), cryogels were produced using a lyophilisation step (after exchange with appropriate solvent, i.e., ultrapure water or tert-butanol), whereas xerogels were produced using convective drying (85°C in air). At last, the dried gels were pyrolyzed under N₂ stream (100 cm³ STP min⁻¹) at 900 °C (5°C min⁻¹, 2h dwell time). The resultant carbon gels were named mA, mC or mX, depending on their way of drying, and “m” standing for the amount of isopropanol in the initial mixture. The texture of the final carbon gels was obtained from N₂ and CO₂ adsorption studies. The adsorption isotherms were then treated using SAIEUS® software (two-dimension non-local density functional theory: 2D-NLDFT) in order to obtain pore size distributions, pore volumes and specific surface areas. The MB adsorption experiments (kinetics and equilibrium studies) were carried out at 3 different temperatures (15, 25 and 45 °C).

Results and Discussion

The synthesis procedure is partly summarized in **fig. 1.a**). Gelation led to brownish and homogenous gels when the amount of isopropanol was between 7.5 and 12.5g. Above and below this range, demixing and phase separation occurred, leading to inhomogeneous gels (**fig. 1.b**). The total pore volume of the carbon gels exhibited a maximum (0.3 cm³ g⁻¹) around 12.5 g of isopropanol in the initial mixture (12.5A material), while the maximum specific area was equal to 920 m² g⁻¹ for the 15A material. The specific area of the 12.5A material was slightly lower (860 m² g⁻¹), but this material exhibited some mesoporosity that has interest when it comes to diffusion-related processes such as adsorption kinetics. Surprisingly, the carbon xerogels, cryogels and aerogels coming from the formulation using 12.5g of isopropanol had very similar textural properties (e.g. 860-950 m² g⁻¹). Thus, in this particular situation, the cheapest and most economical way of drying is the convective

one. As a consequence, the chosen material for MB adsorption assays was the 12.5X.

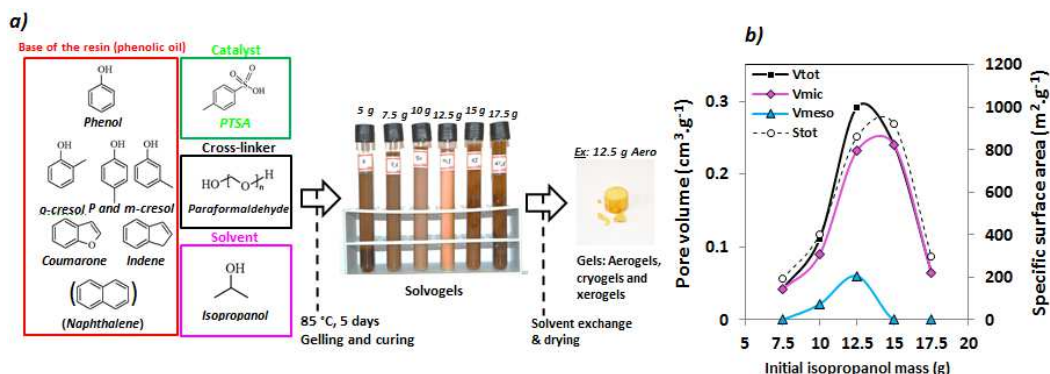


Figure 1. Summary of the synthesis of the gels (a.), and pore volumes (total, micro and mesoporous) and specific areas of the carbon aerogels according to NLDFT (b.).

According to the kinetic studies (not shown here), the MB adsorption process followed a pseudo-second order and exhibited. The isotherms were fitted using Langmuir, Freundlich and Sips models. The adsorbed amounts increased with temperature (fig. 2.a). This rare but already observed behaviour is justified by the fact that the bonds between the adsorbed solvent (i.e., water) and the carbon gel are stronger than those between adsorbed MB and the same carbon gel¹. Thus, even if the adsorption process is still spontaneous ($\Delta G_{\text{ads}} < 0$) (fig. 2.b))², the heat of adsorption (fig. 2.c)) reaches negative values at very low adsorbed amount. This endothermic character tends to confirm the aforementioned observation.

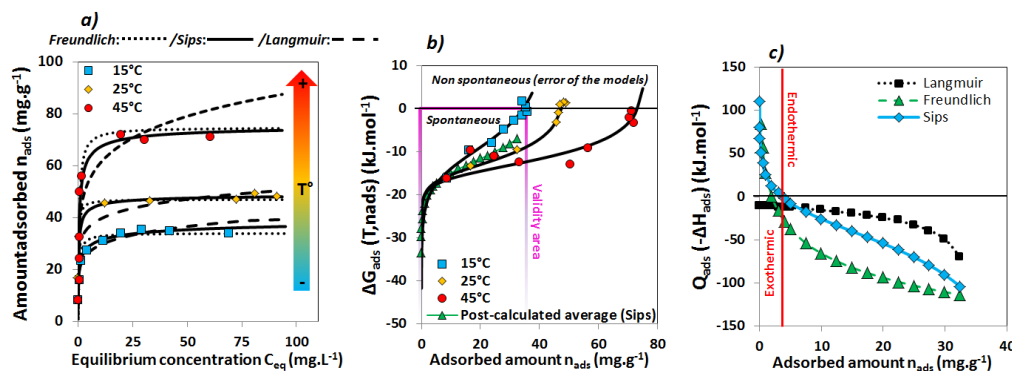


Figure 2. Methylene Blue adsorption isotherms (a.), Gibbs energy of adsorption process depending on adsorbed amount (b.) and heat of adsorption depending on MB adsorbed amount (c.).

Conclusion

Carbon gels precursors were synthesised using phenolic oil in a one-step process. The texture of the best carbon xero-and aerogels were similar ($\approx 900 \text{ m}^2 \text{ g}^{-1}$), leading us to choose the convective way of drying. MB adsorption assays showed that the removal efficiency of the system increased with temperature. This behaviour was justified by an uncommon endothermal adsorption process.

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