

Sujet de thèse 2023: Bourse Ecole Doctorale, Université Claude Bernard Lyon1

Microwave-Regenerable Sorbents-Catalysts. Adsorbant-Catalyseurs régénérables par traitement micro-onde.

Main supervisor

Dr. Frédéric Meunier (HDR)

E-mail: frederic.meunier@ircelyon.univ-lyon1.fr

Co-supervisors

Dr. Corinne Ferronato

E-mail: corinne.ferronato@ircelyon.univ-lyon1.fr

Prof. Akim Kaddouri (HDR)

E-mail: akim.Kaddouri@ircelyon.univ-lyon1.fr

Context.

Indoor and cabin air pollutions by Volatile Organic Compounds (VOCs) represent serious threats to human health. The origins of VOCs are diverse, e.g., furniture, floors, paints, human or animal sources, heating and cooking systems, outdoor pollutants, leading to complex mixtures of alkanes, alkenes, alcohols, aldehydes, aromatics, halogenated compounds and many other compounds. Formaldehyde, benzene, CO, acrolein, acetaldehyde and chloroform are among priority pollutants to be removed from homes, offices and schools ¹. Apart from improving ventilation systems, which also has limits when large temperatures gradients exist between inside and outside, the two main control techniques are based on VOCs destruction and adsorption ^{2,3}.

Destruction techniques (e.g. total oxidation through catalysis⁴, plasma, ozonation, photocatalysis) are typically energy-intensive, costly and some of those may result in the formation of secondary pollutants ². Adsorption can be effective but is limited by the need to replace or regenerate the sorbent. Four main classes of sorbents are defined, activated carbons (AC), metal-organic frameworks (MOF), hyper-crosslinked polymeric resins (HPR) and zeolites ⁵. Each of those has pros and cons in term of cost, stability, trapping efficiency and regeneration. A recent review ³ stressed the work still needed in improving VOCs control systems, in particular, (i) a fundamental understanding of the interaction between sorbents/catalysts and VOCs, (ii) the effect of water on sorption and (iii) combining Sorbent-Catalyst systems using bifunctional materials.

Objectives of the project

This project addresses several scientific shortcomings discussed above and propose innovative approaches to offer new cost-effective solutions in the destruction of VOCs, that may possibly lead to commercial applications.

First, *operando* IR spectroscopy will be combined with traditional sorption/volumetric methods to describe the adsorption of various VOCs in a set of representative sorbents to determine the main individual physicochemical adsorption parameters (sorption heat, isotherms, sites, coordination mode) and adsorption competitions by studying VOCs mixtures. The effects of water will also be investigated in detail, thanks to the high IR response of adsorbed water and hydroxyl groups.

Second, sorbent regeneration will be done by using microwave heating similar to that of a standard kitchen appliance (2.45 GHz), as to develop a practical and inexpensive regeneration method. This technique was already used (under inert atmospheres) over zeolites ^{6,7} and activated carbons ⁸, but needs to be ascertained over MOFs and polymers. The sorbent will be mechanically mixed with a catalyst composed of a support strongly absorbing microwaves and a phase active for total oxidation (Figure 1). The irradiation of the mixture will result in a sharp and rapid temperature increase of the catalyst (and possibly that of the sorbent and VOCs, depending on their dielectric permittivities) that will result in the fast desorption of the VOCs. The desorbed VOCs will then be combusted over the hot catalyst in close contact.

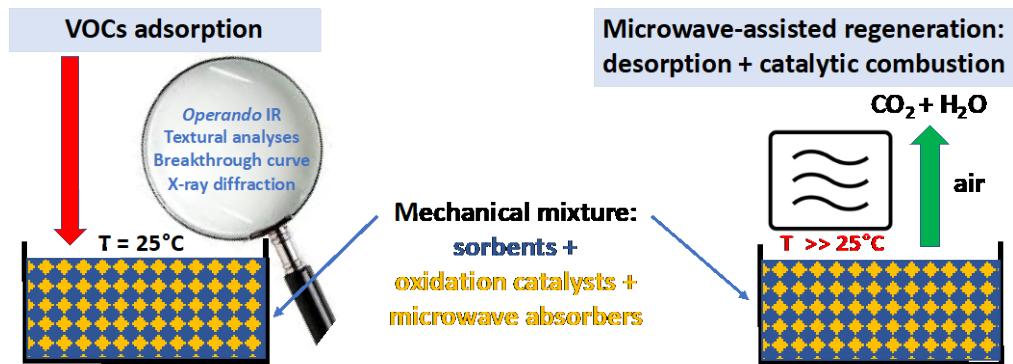


Figure 1. Schematic representation of the project: use various advanced characterization methods to understand VOCs adsorptions in sorbents and the ex situ regeneration in a common microwave oven. The system will consist of sorbents mixed with oxidation catalysts exhibiting high dielectric constants.

To our knowledge, the microwave-assisted VOC desorption combined with catalytic combustion has not yet been reported and offers a fast, practical and inexpensive method to regenerate sorbents. This work would be the first time that such method would be assessed.

The efficiency and durability of the elimination of priority VOCs (i.e., formaldehyde, benzene, CO, acrolein, acetaldehyde and chloroform) on a limited set of sorbents (zeolites, porous polymers, MOFs and Activated carbons) mixed with various catalysts will be determined. A major focus will be to ensure that no harmful secondary products are produced during combustion/regeneration, or at least at acceptable levels based on legal exposition limits. The supervising TEAM are team members of the ATARI group of IRCELYON (<https://www.ircelyon.univ-lyon1.fr/en/team/integrated-thermodynamical-reactional-and-analytical-approaches/>) having complementary knowledge on this topic.

Références :

- ¹ A. Buchmann. **L'Observatoire de la Qualité de l'Air Intérieur (OQAI) : Un outil au service d'une politique de santé environnementale.** Atmos'fair 2017, Lyon.
- ² B. Liu, J. Ji, B. Zhang, W. Huang, Y. Gan, D.Y.C. Leung, H. Huang. **Catalytic ozonation of VOCs at low temperature: A comprehensive review.** J. Hazardous Materials 422 (2022) 126847. <https://doi.org/10.1016/j.hazmat.2021.126847>
- ³ C. Yang, G. Miao, Y. Pia, Q. Xia, J. Wub, Z. Lia, J. Xiao. **Abatement of various types of VOCs by adsorption/catalytic oxidation: A review.** Chem. Eng. J. 370 (2019) 1128–1153. <https://doi.org/10.1016/j.cej.2019.03.232>
- ⁴ F.C. Meunier, L. Cardenas, H. Kaper, B. Smid, M. Vorokhta, R. Grosjean, D. Aubert, K. Dembele, T. Lunkenbein. **Synergy between Metallic and Oxidized Pt Sites Unravelled during Room Temperature CO Oxidation on Pt/Ceria.** Ang. Chem. Int. Ed. 60 (2021) 3799-3805. <https://hal.archives-ouvertes.fr/hal-03105968>
- ⁵ X. Li, L. Zhang, Z. Yang, P. Wang, Y. Yan, J. Ran. **Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process: A review.** Sep. Pur. Tech. 235 (2020) 116213. <https://doi.org/10.1016/j.seppur.2019.116213>
- ⁶ H. Nigar, N. Navascués, O. de la Iglesia, R. Mallada, J. Santamaría. **Removal of VOCs at trace concentration levels from humid air by Microwave Swing Adsorption, kinetics and proper sorbent selection.** Sep. Pur. Tech. 151 (2015) 193–200. <http://dx.doi.org/10.1016/j.seppur.2015.07.019>
- ⁷ Y. Lv, J. Sun, G. Yu, W. Wang, Z. Song, X. Zhao, Y. Mao. **Hydrophobic design of adsorbent for VOC removal in humid environment and quick regeneration by microwave.** Mic. Mes. Mat. 294 (2020) 109869. <https://doi.org/10.1016/j.micromeso.2019.109869>
- ⁸ Y.-T. Chen, Y.-P. Huang, C. Wang, J.-G. Deng, H.-C. His. **Comprehending adsorption of methylethylketone and toluene and microwave regeneration effectiveness for beaded activated carbon derived from recycled waste bamboo tar.** J. Air Waste Manag. Ass. 2020, 70, 616–628. <https://doi.org/10.1080/10962247.2020.1742247>