

## Evaluation of olive pit biochar as a sustainable adsorbent for ammonia emissions

Alejandro Lete\*, Jana Sanz, Rodrigo Cardona, Ángela Millera, Isabel Fonts, Gloria Gea

\* Corresponding author: [alete@unizar.es](mailto:alete@unizar.es)

Thermochemical Processes Group (GPT), Aragón Institute of Engineering Research (I3A), University of Zaragoza, Spain.

*Keywords:* biochar, olive pit, waste valorization, ammonia, adsorption

### Introduction

The agricultural and agri-food sector generates a large amount of low-value, highly available waste, whose proper management in producing areas constitutes a significant environmental and logistical challenge. In Spain, a world leader in olive oil production, olive cultivation generates a considerable volume of by-products, among which the olive pit stands out, with an approximate generation of 400,000 tons per year [1]. Historically, this residue has been mainly used for combustion to generate energy or in the construction sector. However, its valorization through thermochemical processes to obtain higher value-added products represents a promising pathway within the circular economy framework.

Furthermore, intensive livestock farming generates significant environmental problems, being the main source of ammonia (NH<sub>3</sub>) emissions derived from the storage and management of slurry. These emissions contribute to air pollution, soil acidification, and the formation of fine particulate matter [2]. In this context, the use of pristine biochar (without chemical activation) derived from agricultural waste is presented as a low-cost alternative for NH<sub>3</sub> adsorption. This study focuses on the valorization of olive pits through pyrolysis at different temperatures, characterizing the obtained biochars and evaluating their preliminary viability as NH<sub>3</sub> adsorbents for future application in farms and livestock facilities.

### Materials and methods

The starting material was olive pit (OP), which was subjected to a slow pyrolysis process for 30 minutes in a fixed-bed reactor under N<sub>2</sub> atmosphere. To evaluate the influence of pyrolysis temperature on the physicochemical properties of the material, three temperatures were selected: 350, 550, and 750 °C, obtaining the biochars designated as OP-350, OP-550, and OP-750, respectively. The characterization of the raw material and the biochars included a proximate analysis for the determination of moisture, ash, volatile matter, and fixed carbon together with an ultimate analysis focusing on the quantification of C, H, N, and O content. Textural properties were determined through N<sub>2</sub> adsorption-desorption (BET method) and CO<sub>2</sub> adsorption (Dubinin-Radushkevich method) analysis to characterize the generated porosity. Biochar pH was measured by stirring 1 g of biochar with 20 mL of water for 1.5 h. Finally, to study the adsorption potential of the biochars, NH<sub>3</sub> adsorption experiments were designed in two modalities: discontinuous (batch) assays, where the biochars were exposed to a static and saturated atmosphere of an aqueous 30 vol% ammonia solution, and dynamic fixed-bed experiments using 100 cm<sup>3</sup> STP min<sup>-1</sup> of 1,000 ppm of NH<sub>3</sub> stream, with outlet concentration monitored by microGC.

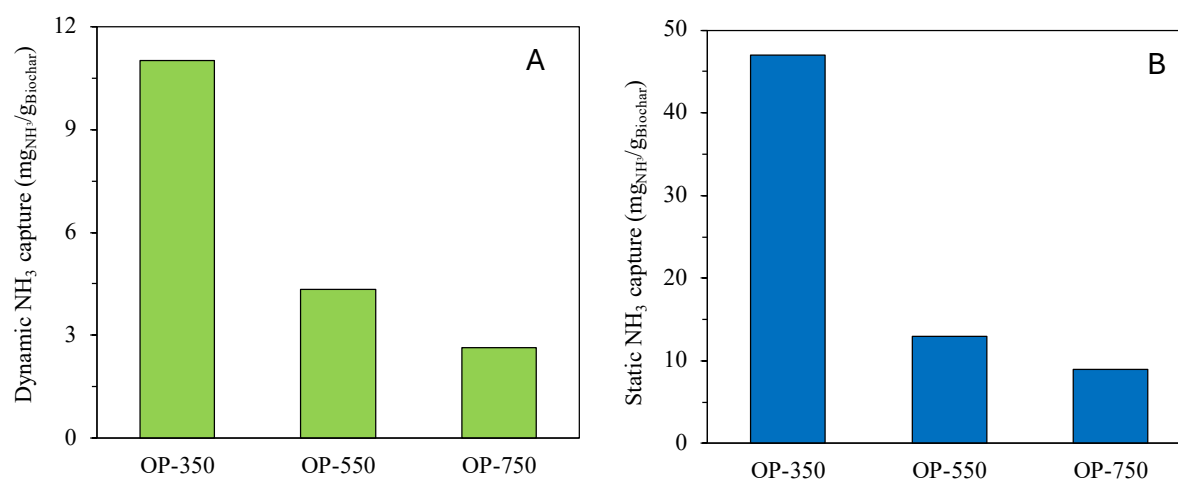
### Results and discussion

Table 1 shows the evolution of the chemical composition of both the raw material and the biochars and the biochars textural properties. The raw material showed 5.4 % humidity, 1.3 % of ash content, 89.2 % volatile matter and 4.1 % of fixed carbon. A clear dependence on the pyrolysis temperature was observed. As the temperature increases from 350 to 750 °C, the volatile matter content drastically decreases due to the thermal degassing of hemicellulose, cellulose, and lignin. Conversely, the percentage of fixed carbon and ash content increase as the carbon and inorganic matrix concentrate. As a consequence, the carbonization process promotes the loss of oxygen and hydrogen, enriching the final solid in carbon, reducing the O/C ratio. The oxygen content is correlated to the presence of oxygenated functional groups [3]. The biochar yield decreased at higher temperatures as the emission of volatile compounds was favored. Textural analysis showed that higher pyrolysis temperature promoted pore development, with OP-750 exhibiting the highest mesoporous (S<sub>BET</sub>) and microporous (S<sub>DR</sub>) surface area, confirming that pristine biochars possess a microporous and ultramicroporous structure.

**Table 1.** Proximate analysis and textural properties of olive pit and OP-biochars.

Sample	C (%)	H (%)	N (%)	O* (%)	O/C ratio	Biochar yield (%)	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>DR</sub> (m <sup>2</sup> /g)
OP (Raw)	49.8	7.1	0.3	42.0	0.84	-	-	-
OP-350	81.0	4.5	0.4	14.1	0.15	37	9	316
OP-550	88.0	3.2	0.4	7.2	0.04	28	83	-
OP-750	95.1	1.3	0.8	1.5	0.02	26	96	709

The adsorption tests revealed an inverse relationship between pyrolysis temperature and NH<sub>3</sub> capture, with both dynamic (Figure 1A) and static (Figure 1B) experiments showing the same trend. The biochar obtained at lower temperatures (OP-350) shows the best performance, reaching 47 mg NH<sub>3</sub> g<sup>-1</sup> in batch tests and 11 mg NH<sub>3</sub> g<sup>-1</sup> under continuous conditions. Despite OP-750 developing the highest surface area, the drastic loss of oxygenated species at higher temperatures compromises the active sites needed for NH<sub>3</sub> adsorption. The better performance of OP-350 is attributed to its higher density of oxygenated functional groups, which facilitate hydrogen bond and acid-base interactions with NH<sub>3</sub> [3]. These findings reinforce the potential of low-temperature biochars as sustainable adsorbents for gaseous NH<sub>3</sub> mitigation.

**Figure 1.** NH<sub>3</sub> adsorption in dynamic (A) and batch (B) experiments for olive pit pristine biochars

## Conclusions

The olive pit emerges as potential precursor for the generation of pristine biochars. The pyrolysis temperature strictly governs the balance between surface chemical properties and textural development. Specifically, lower temperatures promote the retention of oxygenated species, which seems to be the driving force for NH<sub>3</sub> adsorption, whereas higher temperatures significantly enhance a microporous structure. Their application as low-cost adsorbents for NH<sub>3</sub> in livestock facilities represents a key synergy to promote the circular economy between agricultural waste and intensive livestock farming. Preliminary adsorption studies support the viability of this concept and justify further optimization of these materials

## References

- [1] G. Rodríguez, A. Lama, R. Rodríguez, A. Jiménez, R. Guillén, J. Fernández-Bolaños. Olive stone an attractive source of bioactive and valuable compounds, *Bioresource Technology*, 99(12), (2008), 5261-5269. <https://doi.org/10.1016/j.biortech.2007.11.027>
- [2] M. Van Damme, L. Clarisse, S. Whitburn, J. Hadji-Lazaro, D. Hurtmans, C. Clerbaux, P. Coheur, Industrial and agricultural ammonia point sources exposed, *Nature*, 564(7734) (2018), 99. <https://doi.org/10.1038/s41586-018-0747-1>.
- [3] T. Bandoz, C. Petit, On the reactive adsorption of ammonia on activated carbons modified by impregnation with inorganic compounds, *Journal of Colloid and Interface Science* 338(2) (2009) 329-345. <https://doi.org/10.1016/j.jcis.2009.06.039>.