

Wastewater quaternary treatment with vertical-flow constructed wetlands integrated with biochar from sewage sludge

Our research focused on the evaluation of the efficiency of vertical-flow filter systems (VFSs, **Figure 1**) integrated with 2 biochars obtained from sewage sludge coming from different wastewater treatment plants (WWTPs) managed by (Gestione Impianti Depurazione Acque S.p.A., GIDA, Prato, Italy). The VFSs were applied to the quaternary treatment of effluents from the clariflocculation stage of the "Baciacavallo" wastewater treatment plant (GIDA, Prato, Italy), treating mixed domestic-industrial textile wastewater. The experimental systems were installed at the outdoor laboratory of the Department of Chemistry of the University of Florence (Natural Wastewater Treatment Laboratory, NatLab, **Figure 2**) and consisted of 3 laboratory scale mesocosms (high-density polyethylene tanks with height=25 cm and surface area=0.04 m²), according to the following design:

- 1 empty system dedicated to inlet collection, **INLET**;
- 1 system filled with biochar from Calice WWTP sludge, **CAL**;
- 1 system filled with biochar from Baciacavallo WWTP sludge, **BAC**;
- 1 system filled with coarse sand, **CS**.

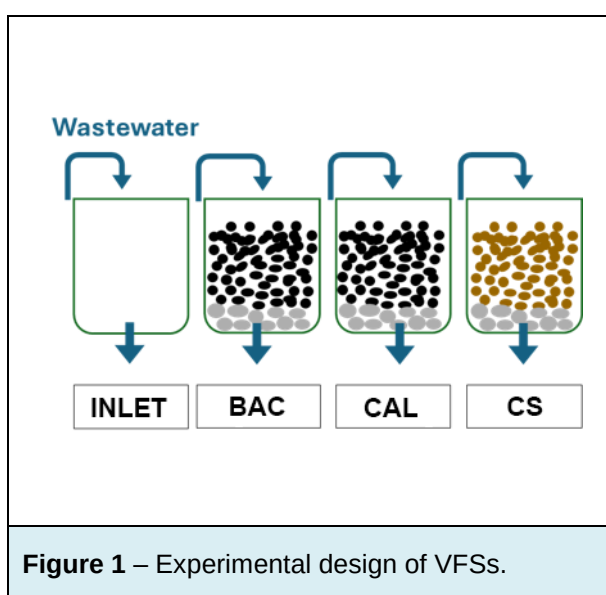


Figure 1 – Experimental design of VFSs.



Figure 2 – View of the VFS experimental setup.

The systems mimicked nature-based solutions, namely vertical subsurface flow constructed wetlands. However, the mesocosms were unplanted, based on results from previous experiments on planted systems (see also Newsletter No. 1)

Both biochars were obtained by pyrolysis in N_2 saturated conditions of dried biological sludge, supplied by GIDA, coming from different WWTPs (i.e., Calice and Baciacavallo). The biochars were chemically activated by washing them with HNO_3 solution, then rinsed with deionized water until constant pH and finally thermally activated in N_2 saturated conditions, as schematically illustrated in **Figure 3**.

The VSSF mesocosms were fed by mean of the "batch" mode with a 6-hour cycle (about 1.2 L/h), repeated 4 times a day, corresponding to a sizing based on the hydraulic loading rate of 200 L/p.e. equal to 0.7 m²/p.e.

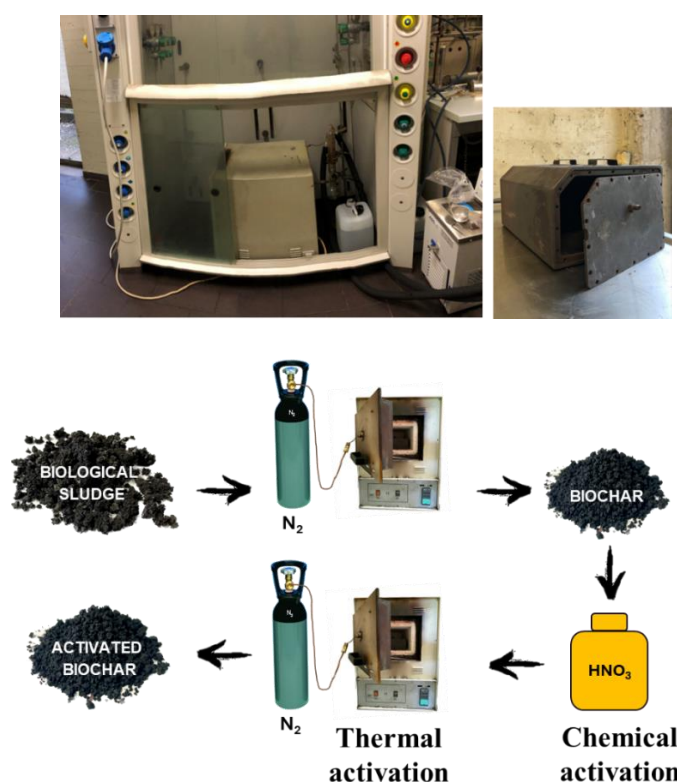


Figure 3 – Biochar production and activation

Conventional parameters (i.e., pH, electrical conductivity, dissolved oxygen, total suspended solids (TSS), chemical oxygen demand (COD), N_{TOT} , NH_4^+-N , $NO_2^- -N$, $NO_3^- -N$, P_{TOT} , PO_4^{3-} as well as absorbances at 254 and 420 nm were weekly determined in inlet and outlet samples. The results obtained, as illustrated by **Figure 4**, showed that BAC and CAL had a statistically higher removal of COD and NH_4^+-N compared to CS. Moreover, the reduction percentage trend of absorbance at 254 and 420 nm highlighted the excellent performance of both biochars throughout the entire working period.

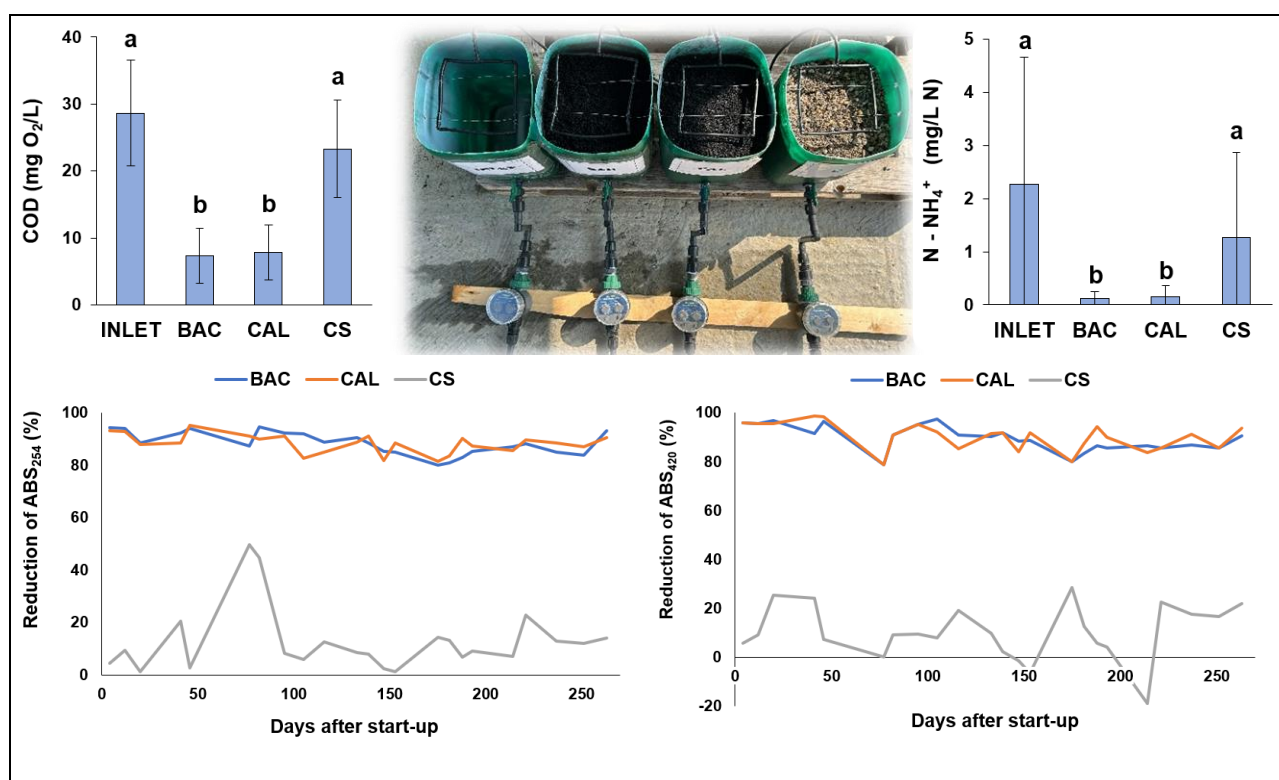


Figure 4 – Results obtained for COD, NH_4^+-N , and absorbance reduction at 254 and 420 nm.

This research involved also the evaluation of the removal efficiency of several emerging organic micropollutants belonging to the classes of **pharmaceutical compounds (PhCs)** and **perfluoroalkyl acid substances (PFAS)**.

The obtained results highlight an almost quantitative removal of PhCs entering the biochar-based VFSs compared to the CS filter. Remarkably, a very high and constant removal throughout the study period was observed also for the most recalcitrant PhCs, such as carbamazepine and venlafaxine (**Figure 5A**), which are two of the target compounds of the 2024/3019 Urban Wastewater Directive. Furthermore, a statistically significant difference ($P < 0.05$) among removals obtained with biochar-based and CS systems was also observed for all PFAS detected in the influent wastewater (**Figure 5B**).

