

Wastewater quaternary treatment with vertical-flow constructed wetlands integrated with biochar from co-pyrolysis of sawdust and sewage sludge

Our study focused on the evaluation of the efficiency of vertical subsurface flow constructed wetlands (VSSF-CWs, **Figure 1**) for the quaternary treatment of effluents from the clariflocculation stage of the "Baciacavallo" wastewater treatment plant (Gestione Impianti Depurazione Acque S.p.A., GIDA, Prato, Italy), treating mixed domestic-industrial textile wastewater. The experimental setup was 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 12 laboratory scale microcosms (high-density polyethylene tanks with height=25 cm and surface area=0.04 m²), according to the following design:

- 3 planted microcosms, with biochar substrate **BC-P**
- 3 unplanted microcosms, with biochar substrate **BC-U**
- 3 planted microcosms, with gravel substrate **G-P**
- 3 unplanted microcosms, with gravel substrate **G-U**

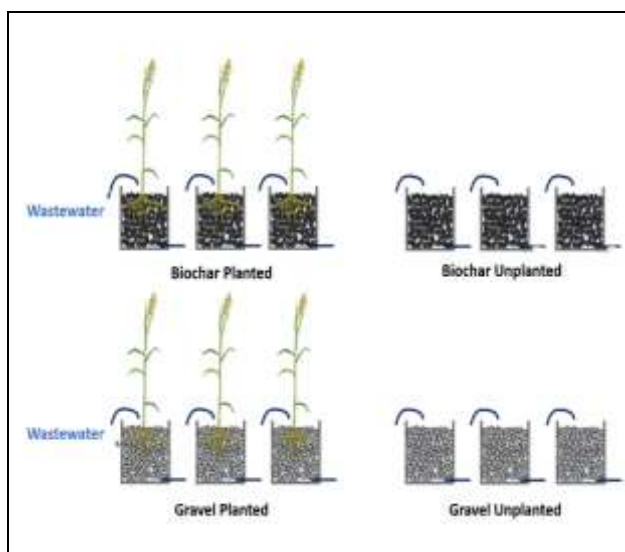
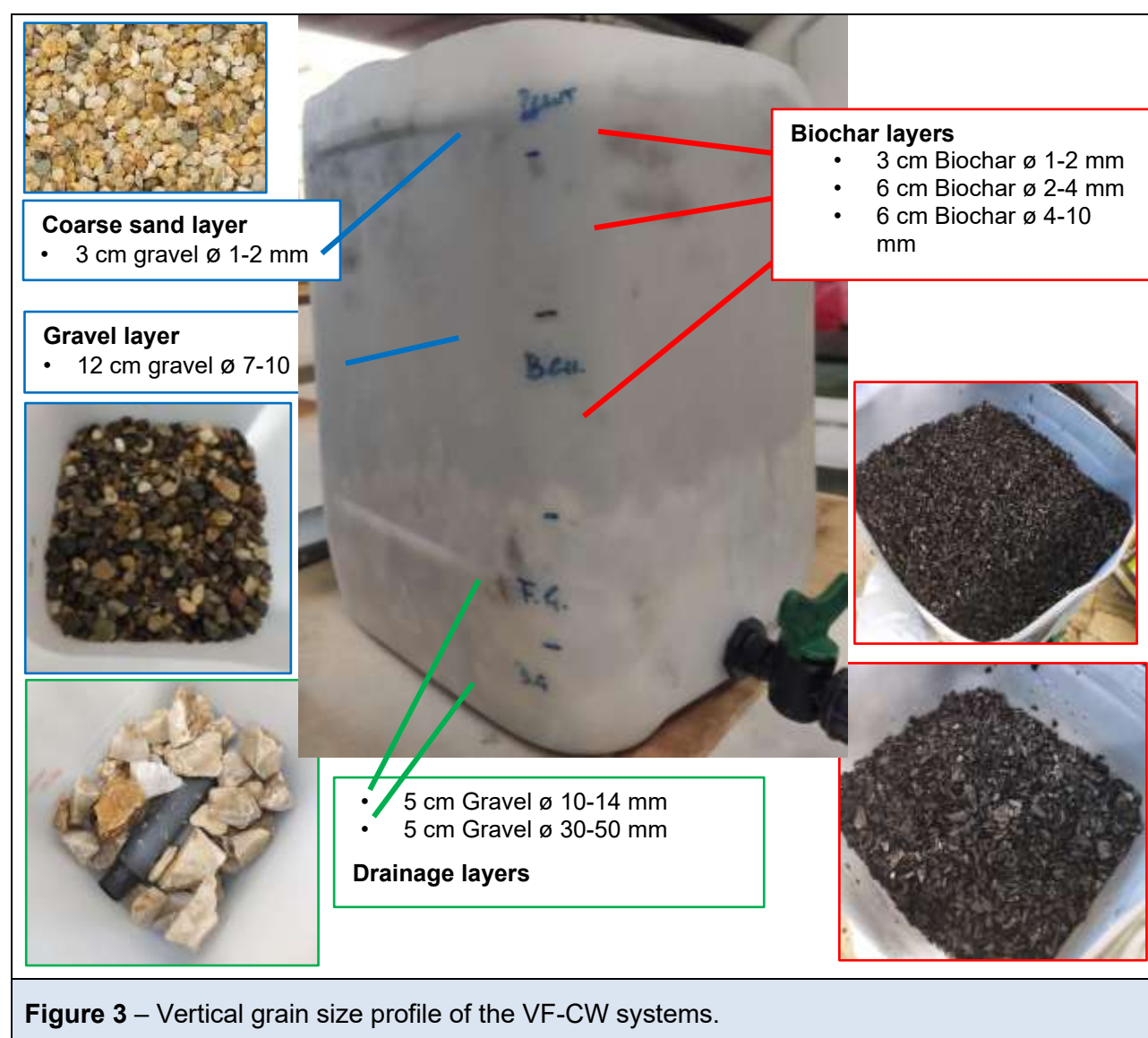


Figure 1 – Experimental design of VF-CWs.

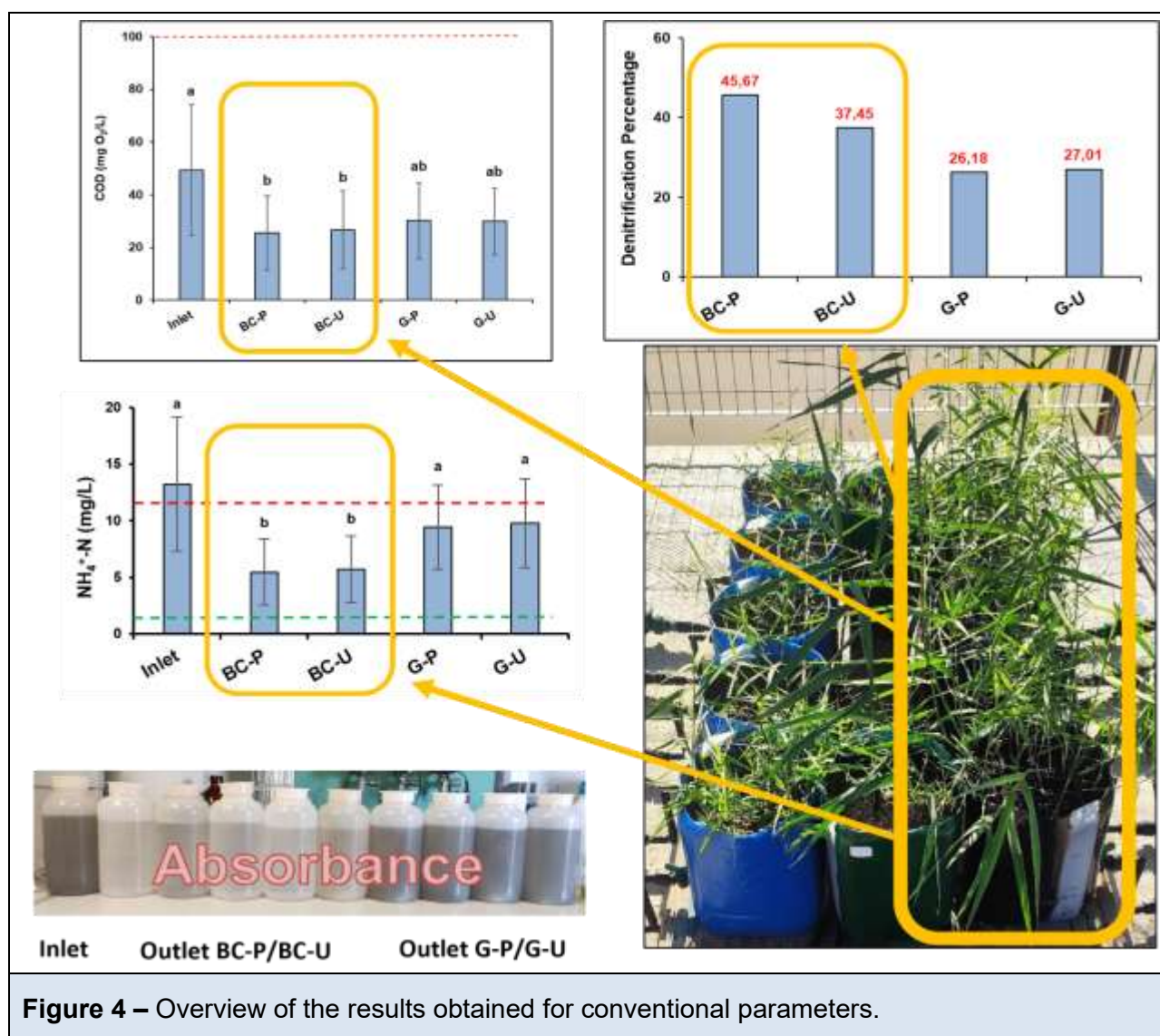


Figure 2 – View of the VF-CW experimental setup.

Six tanks were filled with coarse sand, gravel, and cobblestones according to the European VF-CWs design, by increasing the grain size from top to bottom, while further six tanks were filled with biochar at different granulometry (see **Figure 3**). The biochar was produced by co-pyrolysis of a 70/30 (w/w) mixture of sawdust and biological sludge supplied by Romana Maceri Centro Italia S.r.l. (Civitella in Val di Chiana, Italy) and GIDA, respectively. The biochar was then activated by washing with the commercially available BioDea® acid solution (Bio-Esperia S.r.l., Umbertide, Italy) obtained as a by-product of wood waste gasification and finally washed with deionized water until constant pH.



The mesocosms underwent (i) a loading phase at 21 mL/min for 145 min with the solenoid valve closed, which allowed the complete filling of gravel-based CWs up to the limit of the filling medium, while for biochar-based systems the water level was about 2 cm below the upper limit of the substrate, (ii) a saturation phase for 60 min, (iii) a draining phase, and (iv) a resting phase for 155 min (6-hours cycle, size dimension of 0.7 m²/AE). Conventional parameters (e.g., chemical oxygen demand (COD), NH₄⁺-N, and absorbance at 420 nm, ABS₄₂₀) were weekly determined. COD, NH₄⁺-N showed a statistically higher removal in BC-P and BC-U compared to G-P and G-U (**Figure 4**), highlighting the role of biochar in the removal of these parameters. Absorbance was also strongly removed. Higher denitrification rate was also observed in biochar mesocosms.



This study dealt also with the evaluation of the removal efficiency of a wide group of pharmaceutical compounds (PhCs), some of them included in the European "watch lists" introduced from 2015 to 2022 and in the 2024/3019 European Directive; absorbance at 254 nm (ABS_{254}) was also determined (**Figure 5**).

The removal efficiency of BC-P and BC-U was higher than gravel-based mesocosms throughout the study period (**Figure 5A** and **5E**), even though a more or less rapid decrease in the removal was observed, depending on the analyte considered (**Figure 5F** and **5G**). The removal exhibited by CWs integrated with biochar was almost quantitative since the first days of operation, then undergoing to a decline in the removal during the operation (**Figure 5B** and **5C**). Moreover, biochar-based microcosms did not show negative removals, while G-P and G-U systems gave rise to these erratic events (**Figure 5D** and **5E**).

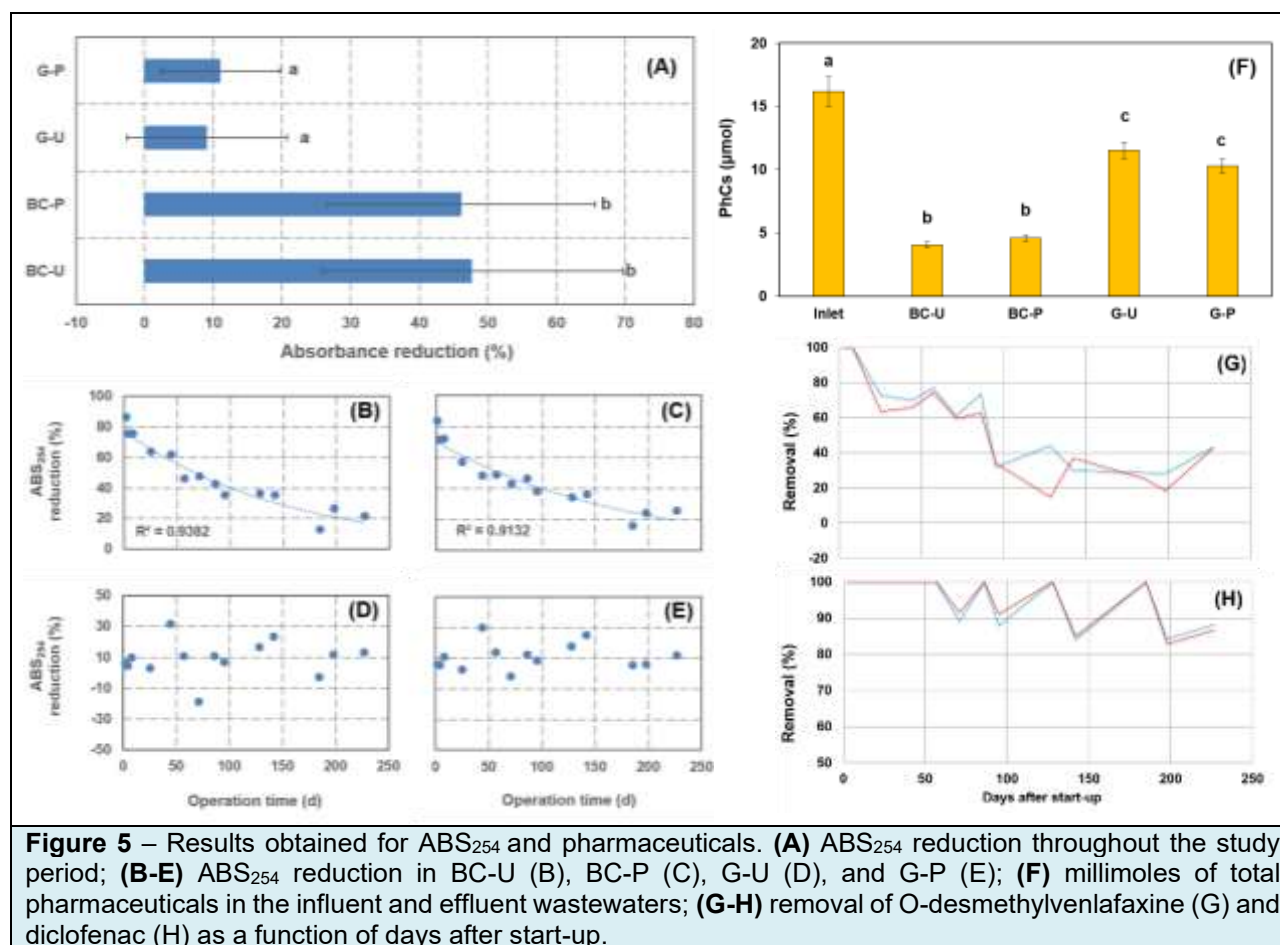


Figure 5 – Results obtained for ABS_{254} and pharmaceuticals. **(A)** ABS_{254} reduction throughout the study period; **(B-E)** ABS_{254} reduction in BC-U (B), BC-P (C), G-U (D), and G-P (E); **(F)** millimoles of total pharmaceuticals in the influent and effluent wastewaters; **(G-H)** removal of O-desmethylvenlafaxine (G) and diclofenac (H) as a function of days after start-up.