

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

Our work focused on the study of the efficiency of vertical-flow constructed wetlands (VF-CWs, **Figure 1**) for the refining 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**

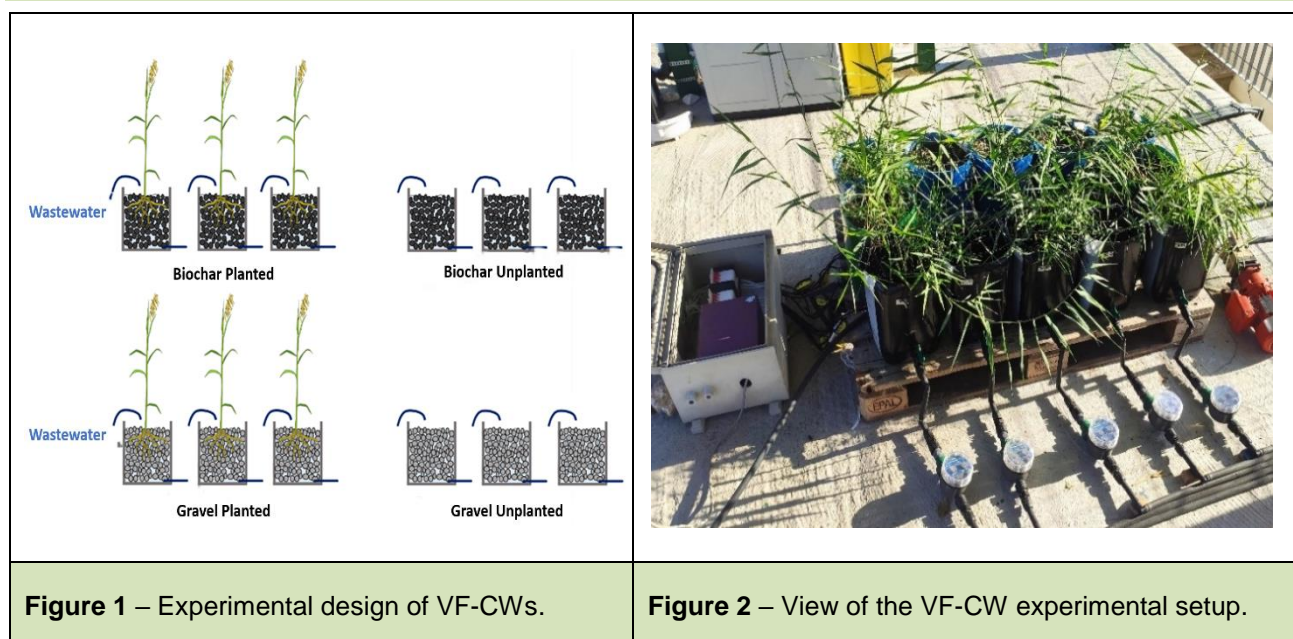


Figure 1 – Experimental design of VF-CWs.

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.

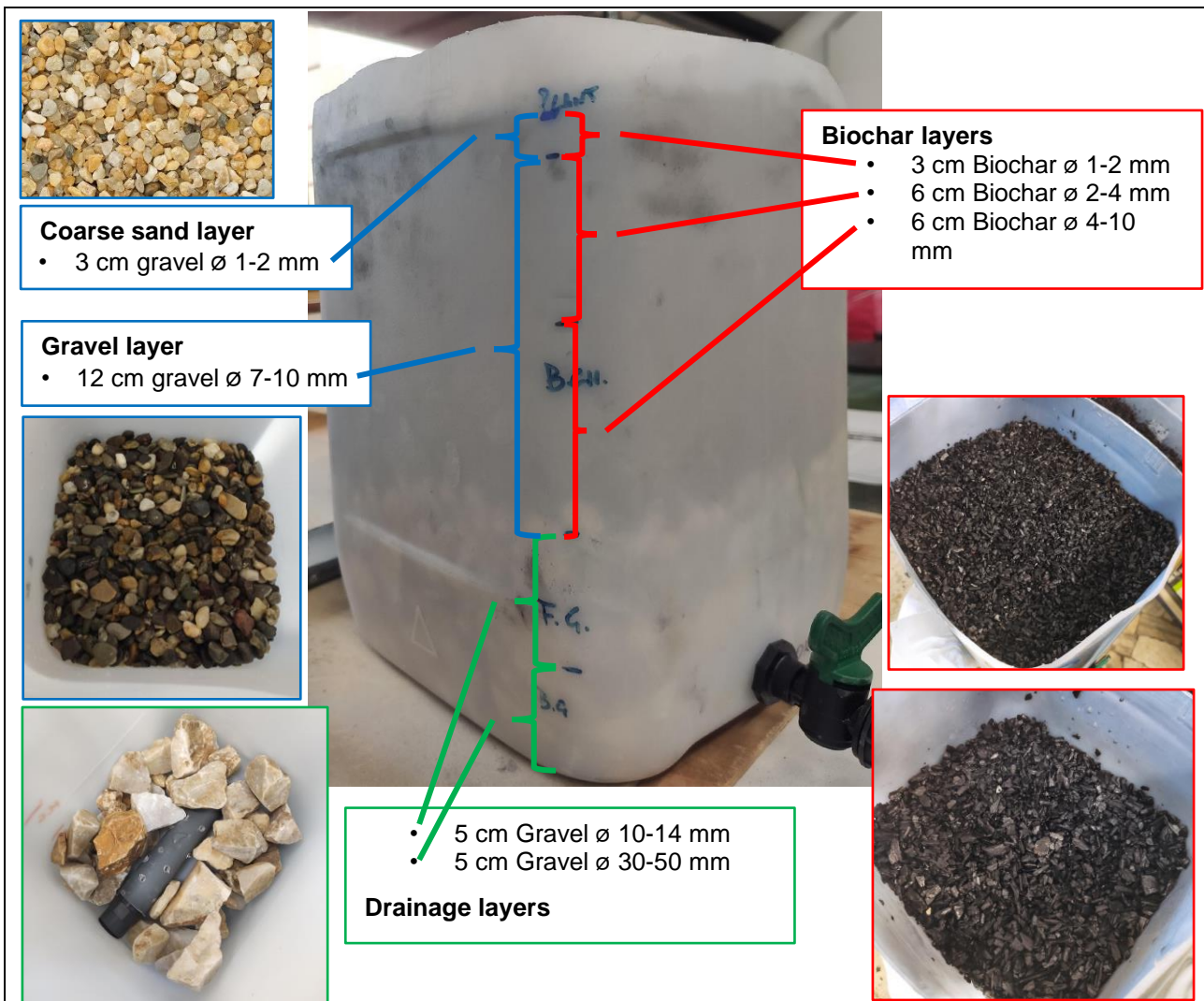
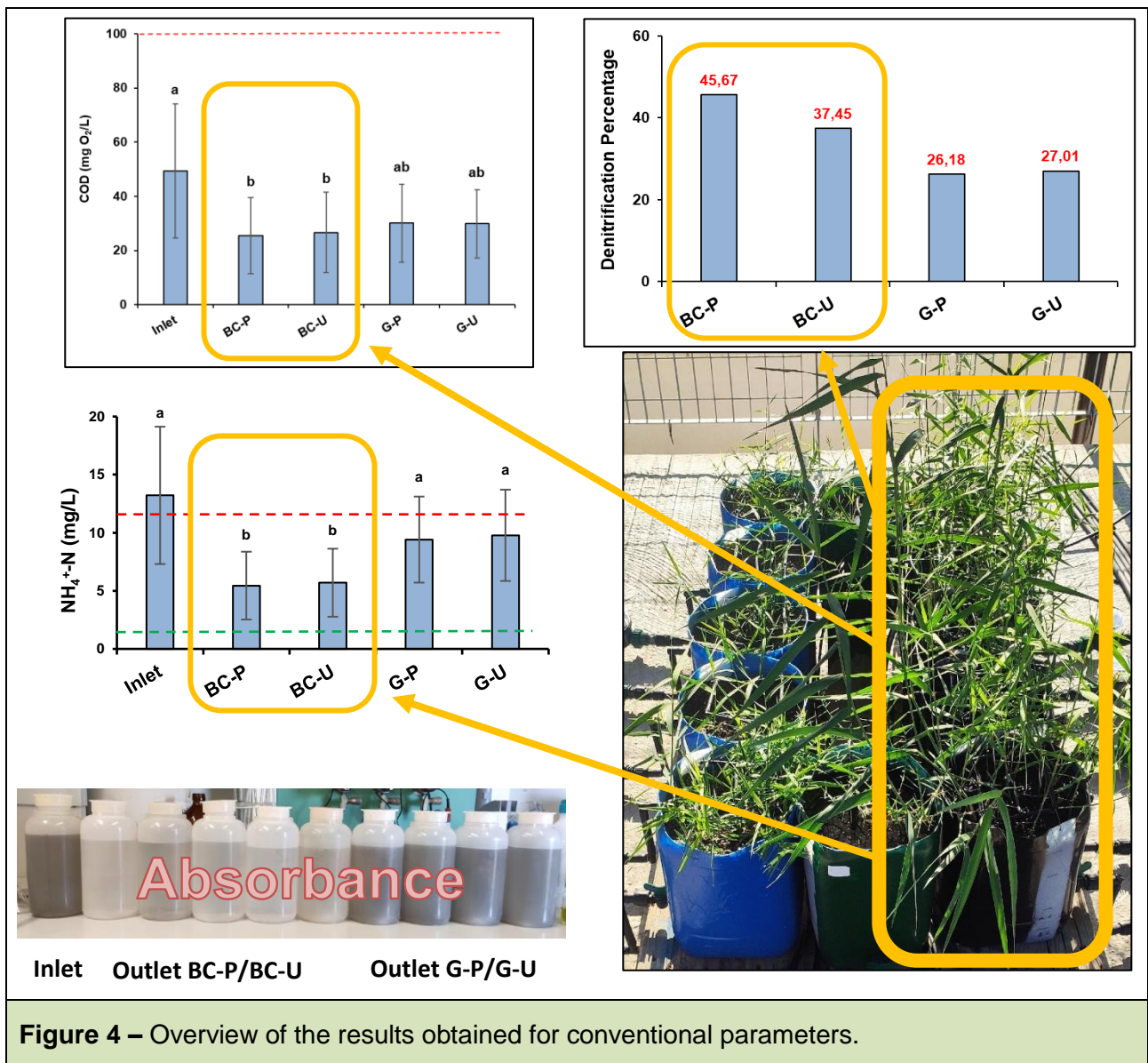


Figure 3 – Vertical grain size profile of the VF-CW systems.

The microcosms were fed in "batch" mode with a 6-hour cycle (about 1.2 L/h), repeated 4 times a day, corresponding to a size dimension of 0.7 m²/AE.

Conventional parameters (i.e., pH, electrical conductivity, total suspended solids (TSS), chemical oxygen demand (COD), NH₄⁺-N, NO₂⁻-N, NO₃⁻-N, PO₄³⁻ as well as absorbances at 254 and 420 nm were weekly determined.

As illustrated by **Figure 4**, COD, NH₄⁺-N, and absorbance at 254 nm and 420 nm, showed a statistically higher removal in BC-P and BC-U compared to G-P and G-U, highlighting the role of biochar in the removal of these parameters. A higher denitrification rate was also observed in biochar-based microcosms.



This study dealt also with the evaluation of the removal efficiency of a wide group of **pharmaceutical compounds**, some of them included in the European "watch lists" introduced from 2015 to 2022.

CWs integrated with biochar showed an almost quantitative removal (85-100%), since the first days of operation (**Figure 5**). For most compounds the removal efficiency was maintained at satisfactory levels ($\geq 70\%$) for about three months, followed by a more or less rapid decrease in the removal, depending on the analyte considered. However, even after about 7 months of operation, the removal efficiency of BC-P and BC-U was higher than in gravel-based microcosms. Moreover, biochar-based microcosms did not show negative removals, while G-P and G-U systems gave rise to these erratic events.

