Chemical activation of substrates: a strategy for improved nutrient and organic matter removal in constructed wetlands

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Highlights:

- First study with a composite of chemically treated construction waste, white cement, and dolomite lime.
- CWs achieved total phosphorus removal efficiencies exceeding 77%.
- CW-WC exhibited nitrogen removal efficiencies greater than 50%.

Keywords: Civil construction waste; Pollutant removal; Support media.

INTRODUCTION

Substrates in constructed wetlands impact plant growth, microbial attachment, and contaminant removal since their physicochemical properties contribute to several pathways (adsorption, retention, degradation) for removing pollutants by enhancing aerobic conditions and microbial interfaces, affecting biofilm formation and community structure. Recent researches explore intensification strategies by combining substrates (shale ceramsite, activated alumina, iron scrap) (Tan et al., 2023) to significantly increase total nitrogen removal. Additionally, modified gypsum boards (de Oliveira Souza et al., 2023) and construction wastes with high adsorption capacity (autoclaved aerated concrete/red clay) (de Carvalho Silva et al., 2024) have demonstrated improvement on phosphorus removal through adsorption and precipitation. These applications associated with plant cultivation and aeration are crucial for optimizing nutrient removal. This innovative research proposes a composite material for enhancing the simultaneous removal of organic matter and nutrients from synthetic wastewater in vertical-flow constructed wetlands filled with a composite from chemically treated construction waste, incorporating white cement and dolomite lime (dominant phosphate adsorbents).

METHODOLOGY

Two rectangular constructed wetlands (0.2 m²) were set up on a microcosm scale using a vertical subsurface flow configuration. The systems were filled with a composite composed of activated red ceramic, white cement (CW-WC), and dolomite lime (CW-DL) and planted with *Eichhornia crassipes* (density of 25 plants m^{-2}) (Figure 1).

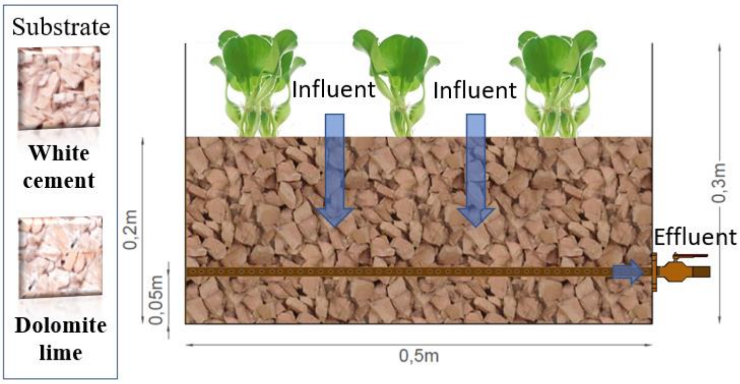

Figure 2 - Schematic of the constructed wetlands systems planted with *Eichhornia crassipes*

These materials were collected before being used in civil construction to prevent leaching of contaminants into the systems. The chemical activation process with white cement and dolomitic lime followed the methodologies described by Cabral et al. (2021) and Kuhn et al. (2023). The CWs were fed manually with synthetic effluent prepared according to De Carvalho Silva et al. (2024) in batch mode in cycles of 48-48-72-hours. Samples were collected after 24 hours of feeding. Liquid temperature (°C) and pH (4500-H+B), dissolved oxygen (DO) (mg L^{-1}) (4500-O B'), oxidation-reduction potential (ORP) (mV) (2580 ORP), chemical oxygen demand (COD) (mg L^{-1}) (5220 D), ammonia nitrogen (N-NH_3) (mg L^{-1}) (4500-NH_3-N C), nitrite (mgN-NO_2^- L^{-1}) (4500-NO_2- B), nitrate (mgN-NO_3- L^{-1}) (4500-NO_3-), and total phosphorus (TP) (mg L^{-1}) (4500-P I) were determined in influent and effluent samples of the CWs, following APHA (2017).

RESULTS AND CONCLUSIONS

The average temperature in the influent and effluent of CW-DL and CW-WC remained around 22.8, 23.4, and 23.5 °C, respectively. After treatment, pH decreased from 7.6 to 7.3 and 7.1, and DO from 1.3 to 0.6 and 0.8 mgO_2 L^{-1} in the effluent of CW-DL and CW-WC, respectively. The systems were predominantly operated in anoxic conditions (-100 to +100 mV) (Matos et al., 2010).

CW-WC (70.8%) achieved higher removal efficiency of COD compared to CW-DL (67.5%), with COD reducing from 171.7 ± 18.2 to 48.0 ± 12.5 mg L^{-1} in CW-WC and 54.8 ± 9.3 mg L^{-1} in CW-DL. The results suggested that both materials have comparable removal capacities, promoting biofilm formation and subsequent organic matter degradation processes. The primary mechanisms for organic matter reduction are adsorption onto substrates and microbial assimilation (Stefanakis & Tsihrintzis, 2012). Table 1 presents temperature, pH, DO, ORP, TA, COD, TN, and TP results.

Samples	Parameter	T	pH	DO	ORP	TA	COD	TN	TP
Influent	Mean	22.8	7.6	1.3	18.3	65.0	171.7[a]	33.5[a]	11.4[a]
	Max.	25.9	8.0	1.4	41.0	69.2	195.9	37.5	12.6
	Min.	21.0	7.0	1.2	-26.0	61.3	147.9	29.8	9.7
	SD	2.0	0.3	0.1	21.0	3.3	18.2	2.6	1.1
CW-DL	Mean	23.4	7.3	0.6	-32.8	98.9	54.8[b]	20.9[b]	1.8[b]
	Max.	26.1	7.4	1.0	-2.0	116.0	64.4	24.4	2.7
	Min.	21.0	6.7	0.3	-43.0	84.8	41.9	17.6	1.5
	SD	2.0	0.2	0.2	12.8	10.7	9.3	2.2	0,5
	E (%)						67.5	33.5	84.4
CW-WC	Mean	23.5	7.1	0.8	-31.5	85.7	48.0[b]	13.8[c]	1.5[b]
	Max.	26.1	7.3	1.7	-5.0	92.6	60.1	15.8	1.5
	Min.	21.2	6.6	0.6	-46.0	78.1	25.0	12.4	1.5
	SD	1.9	0.2	0.1	-5.0	6.2	12.5	1.4	0,2
	E (%)						70.8	56.8	87.8

Table 1 - Values of temperature, pH, DO, ORP, TA, COD, TN and TP (308 days of operation, n = 32). Note: Max – maximum value; Min – minimum value; SD – stardard deviation; E% - removal efficiency (%); T – temperature (°C); pH – hydrogenionic potential; TA – total alkalinity ($mgCaCO_3\ L^{-1}$); DO – dissolved oxygen ($mgO_2\ L^{-1}$); ORP – oxidation-reduction potential (mV); COD – chemical oxygen demand ($mg\ L^{-1}$); TN – total nitrogen ($mgTN\ L^{-1}$); TP – total phosphorus ($mgPO_4^{3-}\ L^{-1}$).

Regarding TN removal, CW-WC achieved higher removal efficiency (56.8%) than CW-DL (33.5%) for the average influent concentration of 33.5 ± 2.6 mg L^{-1}, probably by nitrification, plant assimilation, substrate adsorption, and volatilization as the main acting mechanisms.

Similar TP removal efficiencies were obtained for the CWs, with 84.4% and 87.8% for CW-DL and CW-WC, respectively, for the initial concentration of 11.4 ± 1.1 mg L^{-1}. The chemical activation with white cement and dolomitic lime, rich in Ca^{2+}, intensified TP removal through the electrostatic attraction between PO_4^{3-} and Ca^{2+}, Fe^{3+}, Al^{3+} (Li et al., 2021), leading to the formation of insoluble compounds or the exchange with hydrated metal ions on the surface of the substrates, followed by incorporation into their crystalline structure (Kuhn et al., 2023). The chemical activation of red ceramic provided satisfactory results for COD (> 60%) and TP (> 75%) removal for both materials. However, CW-CW demonstrated a better capacity to remove TN (> 50%). These findings highlight the availability of the chemical activation of substrates as a strategy to improve the performance of these systems in removing carbon and nutrients.

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