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Adsorbent modified constructed wetlands for advanced removal of bulk organics and heavy metals from municipal wastewater effluent†

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Constructed wetlands (CWs) represent a nature-based solution (NBS) for the treatment of wastewater, employing natural processes to mitigate aquatic pollution. Nevertheless, the high specific surface area demand of CWs remains a limiting factor, particularly in urban areas. As the removal of organic and inorganic pollutants is predominantly influenced by the removal mechanisms associated with the selected substrate/adsorbents, this study aims to optimise these processes by hybridising different adsorbents such as biochar, granular activated carbon (GAC) and natural zeolite. Over a period of 18 months, five different approaches were tested, with modifications made to the various layers of the respective CW. Furthermore, the heavy metal (HM) speciation, the behaviour of pollutants and the changing environmental conditions within the wetlands were observed at different filter depths to determine the removal potential of the different adsorbents. The results indicated that the modified CW with biochar, zeolite, and GAC enabled high removal rates of bulk organics (91%) and HMs (Cd: 32%, Cr: 86%, Cu: 92%, Fe: 83%, Ni: 91%, Pb: 43%, and Zn: 96%) with significantly lower hydraulic retention time (HRT) compared to previous studies. This addresses the specific surface area as the main issue of these systems. It was also demonstrated that effective pre-treatment is crucial for maximizing the removal ability of CW systems. Thus, the use of these systems as a polishing technology for the downstream treatment of municipal wastewater is recommended.

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Water impact

The pilot-scale study indicated that modifying and hybridising vertical constructed wetlands with biochar, zeolite and granular activated carbon enables high removal of bulk organics, nutrients and heavy metals with significantly lower hydraulic retention time compared to previous studies. This addresses the specific surface area demand as one of the main limiting factors of constructed wetland systems.

1. Introduction

Access to water is a fundamental human right and a critical determinant of human well-being. As such, it should be readily available and safe for all individuals, irrespective of their background, standing, or economic circumstances.¹ Heavy metals (HMs), (trace) organics, and excess nutrients are among the pollutants that pose substantial threats to aquatic ecosystems and human health. Approximately 40% of the world's rivers and lakes have been found to be polluted with

HMs due to the increase in industrial production, especially in emerging countries.² HMs pose a big threat due to their non-degradable nature and potential transformation into active or toxic forms.³ Some elements, including chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn), play vital roles in biological processes. In contrast, lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are known for their biotoxic properties. Besides allergic reactions, the impact of nickel (Ni) remains under ongoing investigation and is not conclusively determined.^{4,5} Especially As, Cd, Cr, Cu, Hg, Ni and Pb are critical pollutants due to their occurrence in drinking water sources.⁶ Constructed wetlands (CWs) have emerged as a nature based solution (NBS), for cost-effective and largely self-sufficient secondary and tertiary wastewater treatment, leveraging natural processes to mitigate pollution.⁷ Traditionally, CWs have been used to treat diverse wastewater types, including municipal and industrial wastewater, stormwater runoff, and various leachates, demonstrating their

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Table 1 Detailed characteristics of the incorporated adsorbents biochar, GAC, and natural zeolite^{20–30}

Property	Biochar	GAC	Natural zeolite
Origin	Pyrolyzed biomass	Carbonaceous materials (coal, wood, coconut shells)	Naturally occurring aluminosilicate minerals
Porosity/surface area	Moderate porosity, specific surface area $\sim 100\text{--}400\text{ m}^2\text{ g}^{-1}$	Very high porosity, specific surface area $\sim 800\text{--}1500\text{ m}^2\text{ g}^{-1}$	Microporous with moderate surface area $\sim 20\text{--}150\text{ m}^2\text{ g}^{-1}$
Main applications	Soil amendment, contaminant sorption, carbon sequestration	Water and air purification, chemical adsorption	Water purification, ammonia removal, soil remediation
Strengths	Renewable & low-cost, enhances soil health, plant growth and water retention	Very high adsorption capacity, reusable after regeneration	Excellent ion-exchange capacity, selective for ammonium & heavy metals
Weaknesses	Variable quality depending on raw material, lower adsorption than GAC	Relatively expensive in comparison	Lower surface area, slower kinetics, prone to clogging
Environmental impact	Sustainable & carbon-negative	High energy input in production	Environmentally harmless, naturally abundant
Costs	50–1200 \$ per t	800–3000 \$ per t	30–120 \$ per t

effectiveness in contaminant removal. However, to enhance their removal capacity and address the complexities of current pollution, innovative modifications have been introduced in the recent years. To overcome the limited adsorption capacity of conventional CWs, recent modifications incorporating materials such as biochar, GAC, and zeolite have shown promising results.^{8,9} Additionally, to address oxygen limitations in certain CW configurations, artificially aerated systems have been developed to enhance aerobic degradation processes. Furthermore, recirculating CWs have been introduced to increase hydraulic retention time (HRT) time, thereby improving pollutant removal efficiency through prolonged substrate–pollutant interaction.¹⁰ Combining the advantages of vertical and horizontal flow CWs, the invention of hybrid wetlands is another promising approach to further enhance removal capacities.⁵

The mechanisms of heavy metal removal in CWs are complex and involve various pathways such as adsorption, sedimentation, flocculation, cation and anion exchange, complexation, (co-) precipitation, plant uptake and microbial processes (biosorption, bioaccumulation, plant-microbe interactions, and microbe-mediated redox reactions) which also interact synergistically.^{11–13} Sedimented particles can act as secondary adsorbents, while adsorbed metals may later become bioavailable to plants. Microbial processes, particularly under anoxic conditions, facilitate metal precipitation by altering redox conditions and producing sulphides. Additionally, root exudates can mobilize bound metals, indirectly enhancing plant uptake. These interactions highlight the dynamic and interconnected nature of metal removal processes in wetland systems. Previous studies suggest that the removal of organic and inorganic pollutants is mainly influenced by the removal mechanisms associated with the selected substrate/adsorbents.^{5,14,15} In another recent study, adsorption and sedimentation accounted for 99% of HM removal while plant uptake only contributed 0.03%.¹⁶ The substrate not only filters and adsorbs pollutants but also provides a living habitat for diverse microorganisms that form biofilms to eliminate pollutants.¹⁷ Thus, the design and operation of CW systems requires careful selection of substrate/adsorbents materials

based on the properties of the inflow wastewater.¹⁸ Combining and hybridising different adsorbents, such as biochar, GAC, and zeolite, is a promising approach to remove organic and inorganic pollutants due to their unique properties. Detailed information about benefits, main applications and the environmental impacts are given in Table 1. Sedimentation primarily contributes to the removal of particulate-bound metals and is affected by the solubility of the respective HMs and, consequently, pH dependent. Different studies reported that direct plant uptake is rather small with a range of <1–10%.^{5,14} Plants contribute primarily indirectly by oxygenating the rhizosphere, exuding organic chelators and supplying surface area. Notably, many emergent plants develop iron plaques ($\text{Fe}(\text{OH})_3$ deposits) on their root surfaces that absorb metals (*e.g.* *Typha* and *Phragmites* roots remove Pb and Cu *via* their root plaques). Fallen plant litter further adds an organic substrate that traps metals for subsequent sedimentation.¹⁹

Previous studies have shown promising results in adsorbent enhanced CWs. Abedi *et al.* found that a vertical subsurface flow CW (VSSF-CW) in pilot-scale, planted with *Phragmites australis* (common reed) and enhanced with a combination of biochar and zeolite, achieved removal rates of 99.9% for Pb and Mn when treating synthetic wastewater. In contrast, the conventional approach with gravel only achieved 52.4% for Pb and 59.7% for Mn.²⁴ Zhou *et al.* investigated the removal of Pb using zeolite as a substrate in a VSSF-CW and obtained similar results to those previously reported. The removal rates for Cu, Cr, and Zn were 98.2%, 75.1%, and 67%, respectively. However, as the operating time increased, Zn and Cu were desorbed and then re-released.³¹ A study on VSSF-lab-scale-CWs, which used a vermiculite enhanced approach, observed removal rates of $65.7 \pm 1.3\%$ for Cu, $64.3 \pm 1.3\%$ for Pb, and $81.7 \pm 3.3\%$ for Cd during a 60-day operation.³² Another study found that Cd, Cr, Ni, Pb, and Zn accumulated mainly in the upper and middle layers of an unplanted constructed wetland. However, in planted CWs with reed and rush, the accumulation shifted primarily to the top layer. This shift indicates the passive role of plants in constructed wetlands, facilitating the removal of heavy metals.³³ In a separate lab-scale study on the hybridisation of



zeolite and GAC, promising results were observed, although limitations were also identified. The removal potential of zeolites was hampered by high levels of dissolved organic carbon (DOC), ammonium (NH_4^+) and total dissolved solids (TDS).³⁴ This emphasizes the significance of appropriate pre-treatment and the effectiveness of CWs as a polishing technology.

Therefore, this paper focuses on advanced wastewater treatment, examining the potential of various adsorbents to enhance the removal of nutrients, bulk organic matter, and heavy metals, with particular emphasis on the synergistic effects of combining selected materials. Five pilot CWs were tested over a period of 18 months with modifications in different layers of the CWs. The vertical behaviour of pollutants and the changing environmental conditions within the wetlands were also studied at different filter depths to determine the removal potential of the adsorbents in each layer. Furthermore, this paper provides insights into the interactions between the use of a single adsorbent and a combination of adsorbents in a VSSF-CW for the downstream treatment of municipal wastewater.

2. Material & methods

2.1. Site and pilot plant description

The pilot CWs are located at the technical test facility of the wastewater treatment plant (WWTP) Emschermündung in the city of Dinslaken, Germany. The facility is operated by the Emschergenossenschaft/Lippeverband (EGLV). The test facility has been in operation in the current state since 2014 and is designed for the treatment of municipal wastewater of 1000 population equivalents using a conventional activated sludge process.

The pilot plant comprises four wetlands with different modified layers (Fig. 1) as well as a conventional sand-based wetland as benchmark ($\text{CW}_{\text{Conventional}}$) sand with a steep sieve

curve (0/2 mm) was used as filter material in all wetlands, along with 20% w/w broken limestone to prevent acidification. All CWs had a 10 cm gravel (2–8 mm) drainage layer on the bottom with embedded drainage pipes. The modified CWs consisted of 3 different filter layers. The top layer contained sand with 10% w/w of biochar (Biochar PremiumPlus, EGoS GmbH, Germany) for enhanced plant growth, bulk organics removal and water retention. The middle layer was not modified and was set up conventionally with sand and limestone as a pre filtration step before the modified layer. The bottom layer differed in the respective wetlands. The CW_{GAC} contained 30% w/w sand, 20% w/w limestone, and 50% w/w GAC (Cyclecarb 401, Chemviron Carbon GmbH, Germany), whereas the $\text{CW}_{\text{Zeolite}}$ contained 50% w/w of natural zeolite (Zeogran K 80, Zeobon GmbH, Germany) with a Si/Al- ratio of 5.5 instead of GAC. $\text{CW}^+ \text{A}$ and B combined both adsorbents with 25% w/w each, added to 30% w/w sand and 20% w/w limestone.

The wetlands with GAC or zeolite indicated how the removal performance could improve using single adsorbents. $\text{CW}^+ \text{A}$ and B combined the adsorbents to maximise the simultaneous removal of organic and inorganic (trace) compounds. The net filter height of the wetlands excluding the drainage layer was 0.75 m and 0.95 m in $\text{CW}^+ \text{B}$, with a filter surface of 1.2 m². The thickness of the top layer was 15 cm, while the middle and bottom layers were 30 cm thick. In order to elucidate the influence of the filter thickness, the middle and bottom layers of $\text{CW}^+ \text{B}$ have been increased in thickness from 30 cm to 40 cm. Table 2 provides detailed information about the different layers in the respective CWs.

Horizontal, perforated sampling tubes made of polyvinyl chloride (PVC) were included in every layer to investigate the vertical pollutant behaviour and to evaluate the contribution of the different used adsorbents to the pollutant removal as well as the altering environmental conditions in the respective filter depth. The tubes were placed at 0.1 m, 0.4 m,

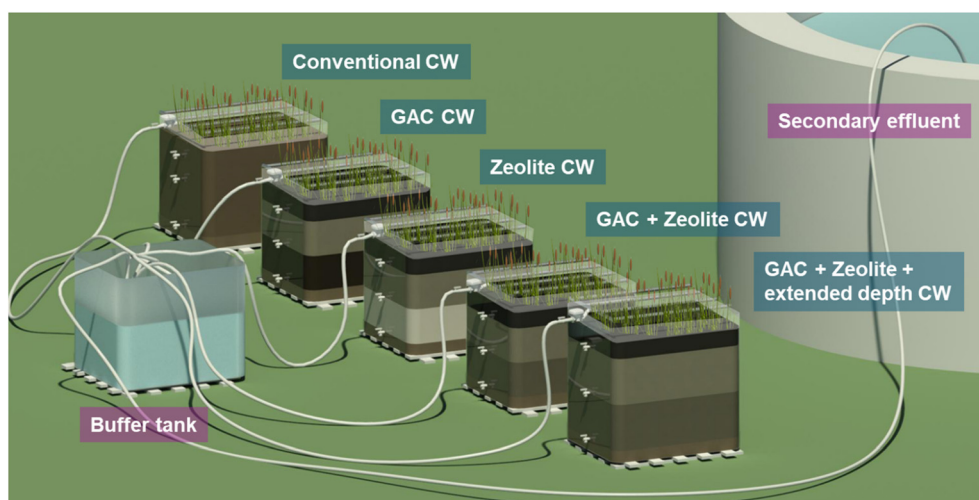


Fig. 1 Constructed wetland pilot setup at the STP Emschermündung in Dinslaken, Germany from left to right: $\text{CW}_{\text{Conventional}}$, CW_{GAC} , $\text{CW}_{\text{Zeolite}}$, $\text{CW}^+ \text{A}$ and $\text{CW}^+ \text{B}$.



Table 2 Layer composition in the different pilot CWs

Layer	CW _{Conventional}	CW _{GAC}	CW _{Zeolite}	CW ⁺ A	CW ⁺ B
Top	Sand + limestone	Sand + biochar	Sand + biochar	Sand + biochar	Sand + biochar
Middle	Sand + limestone	Sand + limestone	Sand + limestone	Sand + limestone	Sand + limestone
Bottom	Sand + limestone	Sand + limestone + GAC	Sand + limestone + zeolite	Sand + limestone + GAC + zeolite	Sand + limestone + GAC + zeolite
Drainage	Gravel	Gravel	Gravel	Gravel	Gravel

and 0.7 m depth in CW_{Conventional}, CW_{GAC}, CW_{Zeolite}, CW⁺ A and in 0.1 m, 0.5 m, and 0.9 m depth in CW⁺ B. The CWs are planted with common reed (*Phragmites australis*) with a density of 7.2 plants per m². The pilot is in operation since September 2022 and was only used for the post-treatment of WWTP effluent. Data included in the present study are from experiments conducted from September 2022 to February 2024.

The effluent from the WWTP was pumped into a storage tank before being distributed with submersible pumps (Lowara DOC 3, Xylem Inc., USA) to the CWs during the feeding events. Hydraulic loading rate (HLR) for each wetland was 144 L d⁻¹ (120 L m⁻² × d) with intermittent feeding of 36 L every 6 h according to the German guideline “principles for the design, construction and operation of constructed wetlands with planted soil filters for the biological treatment of municipal wastewater” to maintain sufficient oxygen supply by providing resting time for the filter.³⁵ A vortex flow sensor was used to measure the flow rates in each wetland. (SV5204, ifm electronic GmbH, Germany).

2.2. Short-term saturation events

Saturation events were simulated on 20 occasions during the test phase. Therefore, the CWs were completely saturated with WWTP effluent, and samples were taken in each filter layer to investigate the vertical pollutant behaviour as well as the changing environmental conditions in the course of the filter depth. Furthermore, the removal of each layer was determined by this approach highlighting the contribution of the different applied adsorbents in overall pollutant removal. Samples were taken from bottom to top after saturation, to maintain a HRT that is as stable as possible.

2.3. Sampling and analysis

Influent and effluent grab samples of the five different CWs were taken on a weekly basis during the feeding phases with 1 L Duran glass bottles. Samples were instantly analysed using a Portavo 907 Multimeter (Knick Elektronische Messgeräte GmbH & Co. KG, Germany) for field water temperature (T) (SE715-MS), dissolved oxygen (DO) (SE715-MS), electrical conductivity (EC) (SE615/1-MS), pH (SE101-MS) and redox potential (SE564X/1-NMSN) directly after sampling. Ammoniacal nitrogen (NH₄-N) was analysed *via* photometry (WTW photoLab S12, Xylem Inc., USA) using cell tests (Test kits, ammonium, Spectroquant, Supelco, Merck GmbH, Germany). Nitrite nitrogen (NO₂-N), nitrate nitrogen (NO₃-N), ortho phosphate (PO₄-P), and sulphate

(SO₄²⁻) were determined by liquid chromatography of ions (930 Compact IC Flex, Metrohm AG, Switzerland) in accordance with DIN EN ISO 10304-1:2009-07.³⁶ For the heavy metal analysis, the samples were directly acidified to a pH < 2 with 1 M nitric acid p.a. (HNO₃) (VWR International, USA) and stored at 4 °C until analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Optima 8300, PerkinElmer Inc., USA) according to DIN EN ISO 11885:2009-09.³⁷ The catalytic oxidation method used for the analysis of total organic carbon (TOC) (TOC-L, Shimadzu Corp., Japan) and total nitrogen (TN) (TNM-L, Shimadzu Corp., Japan) was according to DIN EN ISO 20236:2023-04.³⁸ Samples were analysed for conventional wastewater parameters within the day of collection.

2.4. Heavy metal speciation modelling

To explain and verify the removal and behaviour of the selected HMs, we conducted a pH-dependent speciation analysis using the Software bundle Database/Spina for data input, calculation and visualisation.³⁹ The speciation of HM allowed for a better understanding of the compound's form and, consequently, its solubility. This supports understanding and predictions of co-/precipitation processes in the pilot wetlands. The average WWTP effluent concentrations over the 18-month study duration were used for the modelling.

2.5. Data evaluation

Overall removal was calculated for the whole filter and for the individual layers using eqn (1). HM removal rates were calculated for influent values above the limit of quantification (LOQ). eqn (2) was used to evaluate the removal of each layer in relation to the actual receiving concentration.

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$\text{Removal (\%)} = \frac{C_{\text{overlying layer}} - C_e}{C_{\text{overlying layer}}} \times 100 \quad (2)$$

C_i is the concentration of the CW in the WWTP effluent/inlet of the CW and C_e is the effluent concentration of the respective CW in eqn (1) and the respective layer in eqn (2).

To identify outliers, we calculated upper and lower bounds using eqn (3) and (4).⁴⁰ These equations were applied to all parameters excluding HMs, due to frequent values <LOQ and the overall low effluent concentrations.



$$\text{Lower limit for outliers} = Q1 - 1.5 \times \text{IQR} \quad (3)$$

$$\text{Upper limit for outliers} = Q3 + 1.5 \times \text{IQR} \quad (4)$$

where $Q1$ and $Q3$ are the lower and upper quartiles, and the interquartile range (IQR) is the distance between $Q1$ and $Q3$.

The Student's t -test was used to identify significant differences between the average removals of the different wetlands. Pearson correlation coefficients were calculated to identify relationships between heavy metal concentrations and removal with influent concentrations, environmental conditions, filter depth and $\text{NH}_4\text{-N}$ concentrations. The significance of the Pearson correlation was subsequently checked by the Student's t -test. Results were significant at $p \leq 0.05$.

3. Results and discussion

3.1. Removal of conventional wastewater contaminants

The CWs were fed with WWTP effluent which leads to variations in inflow concentrations over the experiment duration. The mean concentrations and removal rates of the conventional wastewater parameters are given in Table 3. **Bulk organics:** TOC removal was high in the GAC-containing wetlands (85–92%). $\text{CW}_{\text{Zeolite}}$ achieved a TOC removal of $73 \pm 11\%$ whereas $\text{CW}_{\text{Conventional}}$ just removed $49 \pm 11\%$ which is caused by the lower specific surface area of sand compared to GAC, zeolite, and biochar. Furthermore, the biochar in the modified wetlands also increased the hydraulic retention time (HRT), leading to longer contact times with the adsorbents.⁴¹ Nevertheless, $\text{CW}_{\text{Zeolite}}$ had lower TOC removal in comparison to the other modified wetlands. Zeolites have pores that are uniformly sized, ranging from 0.4 to 1.3 nm. However, TOC and even DOC constituents are typically larger molecules. Therefore, effective adsorbents for these applications require pores in the lower meso-scale range (2–

50 nm). The microporous structure of zeolite causes pore blockage with increased loading. This leads to slower intraparticle diffusion and, consequently, slower kinetics compared to GAC.⁴² Thus, the effectiveness of zeolites in removing bulk organic substances is constrained by their smaller pore size of 0.4 nm, which can result in faster pore clogging.⁴³ **Nitrogen:** TN removal varied widely during the test phases, mainly due to nitrification processes, resulting in highly variable TN removal (Fig. 2). As $\text{NH}_4\text{-N}$ removal exceeded 90% in all pilots, $\text{NO}_3\text{-N}$ was the main N-species in the effluent of the CWs (Fig. S2†). This concludes sufficient nitrification but incomplete denitrification which is consistent with the high DO concentrations $>9.5 \text{ mg L}^{-1}$ in all pilot wetlands. The relatively low carbon content in the WWTP effluent and thus the scarcity of an electron donor source ($10.42 \pm 4.53 \text{ mg L}^{-1}$) further limited the denitrification potential in the pilot CWs. Especially in the warmer months from May–August ($10.8\text{--}22.0^\circ\text{C}$), $\text{NO}_3\text{-N}$ concentrations in the effluent exceeded influent concentrations on monthly average values. It is important to note that the similar TN and $\text{NO}_3\text{-N}$ removal was observed in the GAC-containing wetlands in particular. This leads to the conclusion that the porous structure of GAC provided a habitat for microorganisms, including nitrifying bacteria. While GAC is typically introduced to enhance pollutant adsorption, the nitrogen-containing functional groups naturally present in some types of GAC may desorb or leach into the water, further contributing to TN increase. However, the average TN removal was only negative in $\text{CW}_{\text{Conventional}}$ ($-3 \pm 45\%$).

Compared to the WWTP effluent, all CWs showed an increase in DO concentrations and redox potential in their respective effluents, indicating aerobic conditions due to sufficient resting times between feeding events. This also resulted in high nitrification, leading to an average $\text{NH}_4\text{-N}$ removal of $>90\%$. EC in the GAC-containing ($747\text{--}792 \mu\text{S cm}^{-1}$)

Table 3 Operational conditions, average concentrations and removal rates (η) of selected conventional wastewater parameters from 09.2022 to 02.2024 ($n = 36\text{--}48$)

	WWTP effluent	$\text{CW}_{\text{Conventional}}$	CW_{GAC}	$\text{CW}_{\text{Zeolite}}$	$\text{CW}^+ \text{ A}$	$\text{CW}^+ \text{ B}$
Temperature ($^\circ\text{C}$)	12.94 ± 5.21	12.01 ± 5.64	12.09 ± 5.80	11.90 ± 5.87	12.01 ± 5.87	12.39 ± 6.00
DO (mg L^{-1})	8.25 ± 1.55	10.27 ± 2.02	9.78 ± 1.84	10.66 ± 2.08	10.18 ± 2.02	10.10 ± 2.03
pH (–)	7.19 ± 0.47	7.39 ± 0.19	7.17 ± 0.29	7.48 ± 0.21	7.26 ± 0.27	7.21 ± 0.37
EC ($\mu\text{S cm}^{-1}$)	654 ± 132	652 ± 149	781 ± 211	661 ± 183	747 ± 219	792 ± 196
Redox (mV)	146 ± 72	160 ± 45	187 ± 58	184 ± 49	193 ± 51	197 ± 40
TOC (mg L^{-1})	10.42 ± 4.53	5.13 ± 1.12	1.51 ± 1.54	2.99 ± 1.53	0.95 ± 1.09	0.91 ± 1.32
η_{TOC} (%)		49 ± 11	85 ± 14	73 ± 11	91 ± 8	92 ± 5
TN (mg L^{-1})	7.16 ± 3.61	5.79 ± 2.72	4.39 ± 3.16	5.59 ± 3.89	4.52 ± 3.02	3.42 ± 3.13
η_{TN} (%)		14 ± 31	38 ± 38	27 ± 35	38 ± 39	55 ± 32
$\text{NH}_4\text{-N}$ (mg L^{-1})	1.60 ± 3.41	0.04 ± 0.19	0.02 ± 0.04	0.02 ± 0.03	0.01 ± 0.01	0.01 ± 0.01
$\eta_{\text{NH}_4\text{-N}}$ (%)		91 ± 16	93 ± 9	93 ± 8	95 ± 6	96 ± 5
$\text{NO}_2\text{-N}$ (mg L^{-1})	0.08 ± 0.11	0.05 ± 0.19	0.01 ± 0.01	0.01 ± 0.02	0.01 ± 0.01	0.01 ± 0.04
$\eta_{\text{NO}_2\text{-N}}$ (%)		94 ± 15	96 ± 11	94 ± 17	98 ± 6	98 ± 4
$\text{NO}_3\text{-N}$ (mg L^{-1})	5.32 ± 2.46	5.51 ± 2.85	4.51 ± 3.45	4.68 ± 2.82	4.65 ± 3.38	3.42 ± 3.59
$\eta_{\text{NO}_3\text{-N}}$ (%)		-3 ± 45	14 ± 62	17 ± 41	7 ± 70	44 ± 47
$\text{PO}_4\text{-P}$ (mg L^{-1})	0.95 ± 0.69	0.61 ± 0.42	0.22 ± 0.27	0.60 ± 0.41	0.30 ± 0.28	0.25 ± 0.25
$\eta_{\text{PO}_4\text{-P}}$ (%)		24 ± 51	71 ± 28	27 ± 47	62 ± 33	72 ± 25
SO_4^{2-} (mg L^{-1})	102 ± 30	102 ± 34	105 ± 33	104 ± 34	102 ± 33	103 ± 32



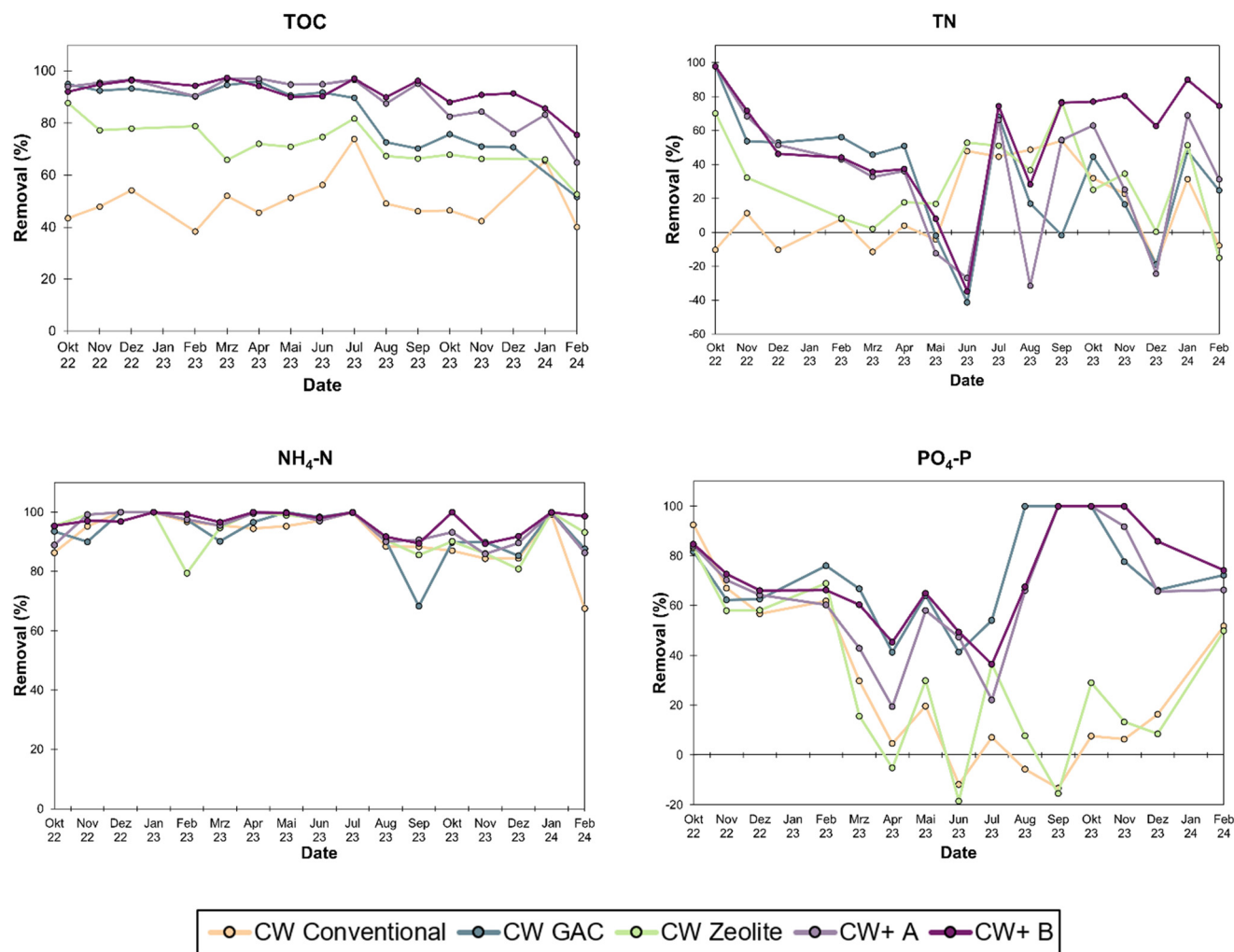


Fig. 2 Average monthly removal rates of TOC and selected nutrients. Outliers were excluded for the calculation.

wetlands was slightly higher in comparison to CW_{Conventional} ($652 \pm 132 \mu\text{S cm}^{-1}$) and CW_{Zeolite} ($661 \pm 183 \mu\text{S cm}^{-1}$). **Phosphorus:** PO₄-P removal showed no significant difference between CW_{Conventional} ($24 \pm 51\%$) and CW_{Zeolite} ($27 \pm 47\%$), but considerably higher removal in CW_{GAC} ($71 \pm 28\%$), CW⁺ A ($62 \pm 33\%$) and CW⁺ B ($72 \pm 25\%$). The lower phosphate removal capacity of zeolite is based on the negative surface charge due to the substitution of aluminium for silicon in their crystal structure and is in accordance with prior studies.⁴⁴ The direct adsorption potential of GAC for phosphorus removal depends on the surface charge. At the point of zero charge (pH_{pzc}), the surface charge of the GAC is neutral. Below this value, the surfaces become positively charged due to the protonation of functional groups, such as amines. At pH values above this point, the electric charge of the GAC becomes negative due to the deprotonation of functional groups, such as phenols and carboxylic acids.⁴⁵ Although the GAC has limited properties for directly adsorbing dissolved phosphorus within the pH range of the pilot testing, it can be used as a filter material to retain suspended solids and precipitated phosphorus. This results in low phosphorus concentrations.⁴⁶ The addition of limestone

stabilized the pH in all CWs and no pH drop due to nitrification was observed during the 18 month of operation.

3.2. Heavy metal removal

All selected HMs were detected in the STP effluent. The average effluent concentrations of the WWTP over the experiment duration were $0.4 \pm 0.6 \mu\text{g L}^{-1}$, $1 \pm 1 \mu\text{g L}^{-1}$, $18 \pm 44 \mu\text{g L}^{-1}$, $59 \pm 43 \mu\text{g L}^{-1}$, $33 \pm 8 \mu\text{g L}^{-1}$, $6 \pm 9 \mu\text{g L}^{-1}$ and $41 \pm 21 \mu\text{g L}^{-1}$ for Cd, Cr, Cu, Fe, Ni, Pb and Zn respectively (Fig. 3). It is important to consider that analytical uncertainties increase as concentrations approach the LOQ, particularly for Cd and Cr due to their low concentrations.⁴⁷ In regard to water reuse, guidance is available through DIN 19684-10, which provides tolerance ranges for various metals and semi-metals in irrigation water with respect to phytotoxic effects.⁴⁸ According to this standard, the STP effluent concentrations of the measured HMs were below guideline values. Nevertheless, the CWs further reduced these concentrations.

The pH of the STP effluent and the effluents of the CWs ranged between 7.2 and 7.5. This is important for evaluating



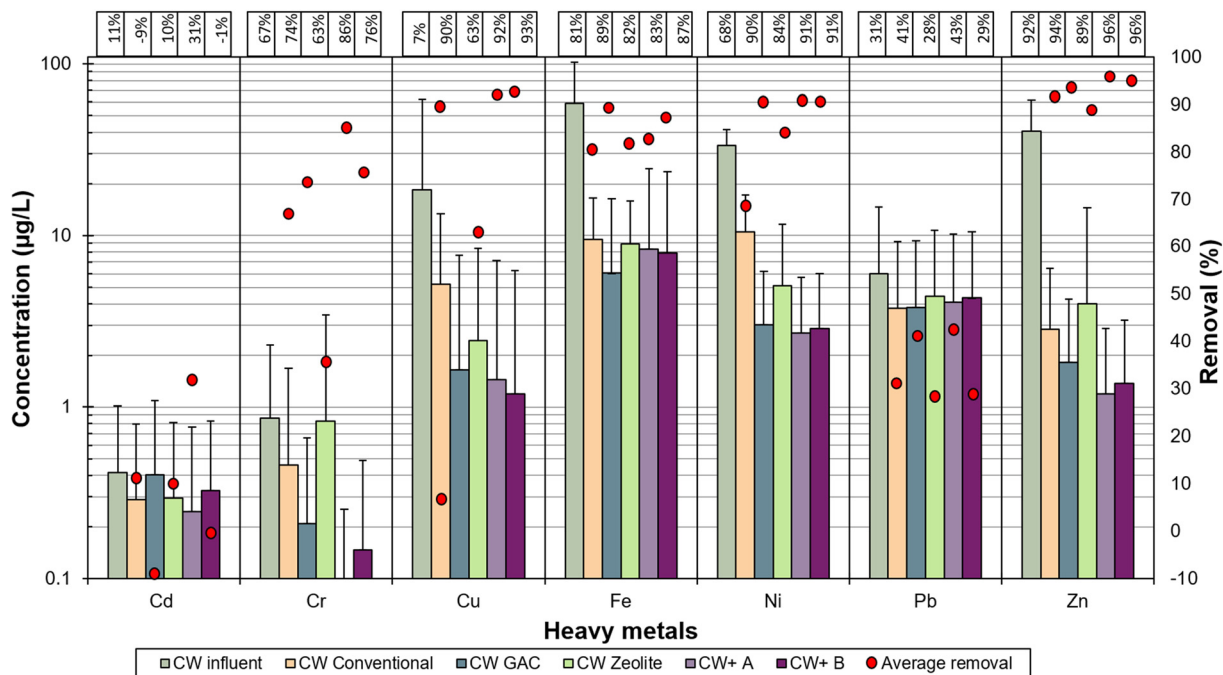


Fig. 3 Average concentrations in influent and CW effluents and removal of heavy metals in the CW influent and the effluent of the respective CWs with standard deviations ($n = 24$). The values indicated above the graph represent the average removal rate of the respective CWs in the order as depicted in the figure from left to right.

the modelling data shown in Fig. 4. **Cd**: average removal of Cd was the lowest among the measured HMs. The highest removal rate was achieved in $CW^+ A$ (32%), while the lowest was in CW_{GAC} with -9%, indicating desorption effects. It should be noted that the low influent concentrations into the wetlands increase the margin of error, as 14 out of 24 were below LOQ in the STP effluent. According to the modelling, Cd predominantly exists as the divalent cation Cd^{2+} . **Cr**: the combined adsorbent approaches $CW^+ A$ and B achieved high Cr removal rates, with 86% and 76% respectively. CW_{GAC} also achieved a removal rate of 74%. However, the wetland containing zeolite only removed 36% of Cr, which was even lower than the removal rate of 67% achieved by the conventional wetland. A previous study which also used zeolite as an adsorbent indicated lower removal of Cr (75%) compared to Pb (100%) and Cu (98%) which were all mainly removed by filtration.³¹ Within the pH range of the experiment, Cr was present as the crystalline zincochromite ($ZnCr_2O_4$). As Zn was not measured in all samples, it was also present as the poorly soluble hydroxide $CrOH^{2+}$ according to the modelling. Hence, the main removal process of Cr under the given conditions are precipitation and filtration. Competitive adsorption and ion-exchange effects on zeolites with other cationic compounds, such as NH_4-N or HMs, with a rerelease of Cr may be the cause for the lower removal in this study compared to the conventional sand wetland.

Cu: Cu removal in the conventional wetland did not exceed 7% and was significantly higher in the modified wetlands ($CW_{Zeolite}$ 63%, $p < 0.05$; CW_{GAC} 90%, $p < 0.01$; $CW^+ A$ 91%, $p < 0.01$; $CW^+ B$ 93%, $p < 0.01$). The low average removal in

$CW_{Conventional}$ is mainly due to the re-release of Cu, resulting in negative removal in 6 out of 15 analyses. In the pH range between 7–8 the speciation of Cu is Cu^{2+} and insoluble copper(II) oxide (CuO) indicating precipitation, filtration, adsorption and ion-exchange as main removal mechanisms. Furthermore, bioavailable HMs such as Cu tend to create complexes with fulvic acid and humic acid as well as other heterogeneous polyligands, which leads to the removal of these compounds due to filtration and adsorption.⁴⁹ Cu removal in VSSF-CWs has been studied extensively. It is important to note that the results of these studies varied widely. Previous research has shown that the use of biochar, zeolite, and biosorbents did not result in Cu removal above 1%.⁸ However, when vermiculite was used as a modification, removal rates of up to 66% were achieved.³² Additionally, Zhou *et al.* reported a 98% Cu removal rate in a zeolite-containing wetland.³¹ **Fe**: Fe was detected in the highest concentrations up to 0.1 mg L^{-1} in the STP effluent but well removed in all wetlands (81–89%). Under the current pH conditions, iron precipitates primarily as insoluble ferric oxide, resulting in subsequent filtration. This process is further enhanced by the aerobic conditions induced by the 6 h resting between the feeding events, facilitating precipitation as oxides, hydroxides and oxyhydroxides.⁵⁰ **Ni**: difference in removal in $CW_{Conventional}$ (68%) compared to the modified wetlands was observed for Ni ($CW_{Zeolite}$: 84%; CW_{GAC} , $CW^+ A$ and B 91%). At a neutral pH, nickel occurs mainly as soluble Ni^{2+} . This form is stable in water due to its ability to form complexes with inorganic and organic ligands, as well as its association with suspended soil colloids.⁵¹ As the pH increases, it becomes



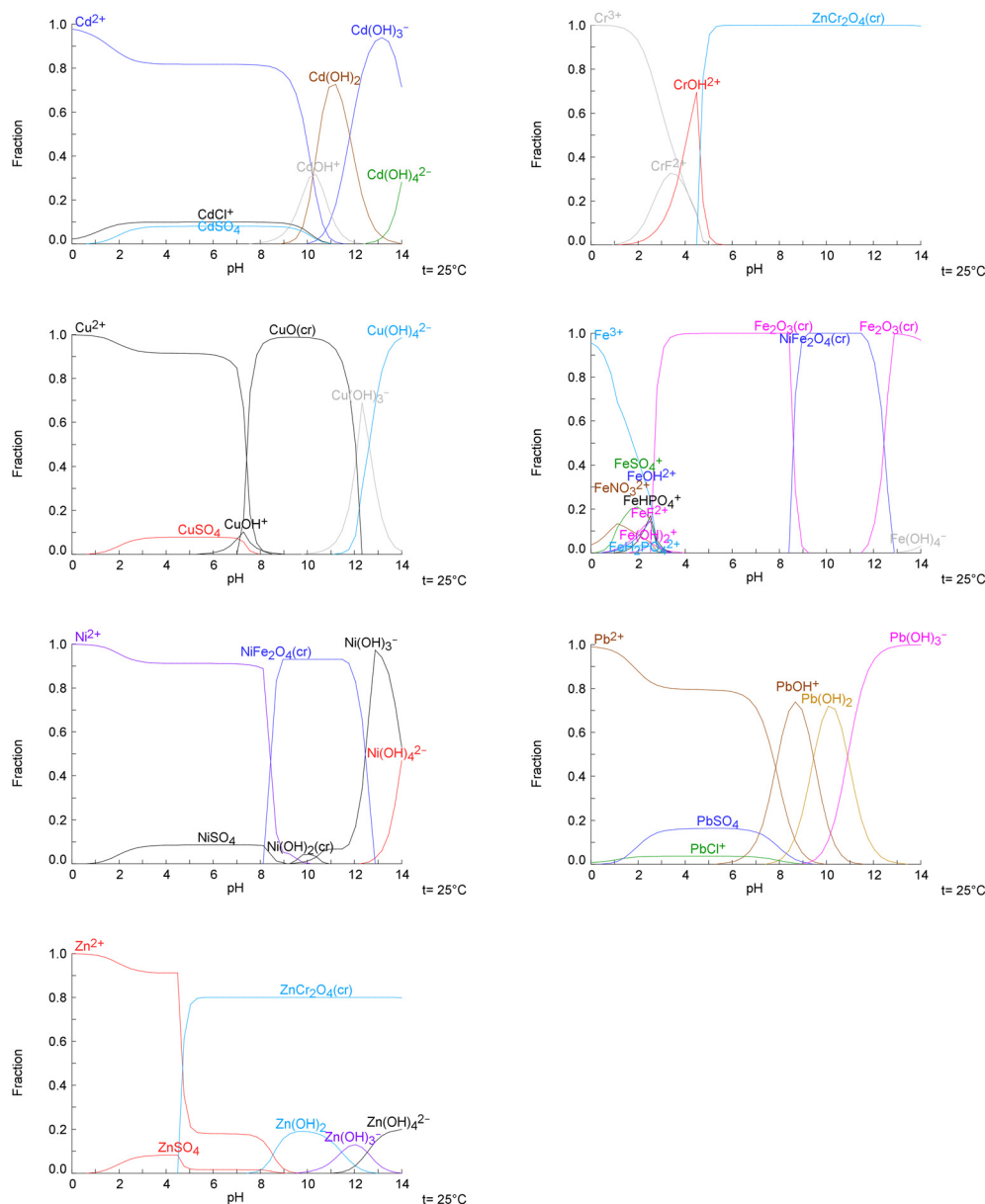


Fig. 4 Modelling the speciation of the investigated heavy metals in dependency of the pH. The used input data for the modelling were the average concentrations over the duration of the experiment.

abundant as $\text{Ni}(\text{OH})_2$ or bound to insoluble Fe-oxide, while $\text{Ni}(\text{OH})_3^-$ occurs mainly in high alkaline conditions. The behaviour of Ni in CWs is affected by redox conditions, which can alter its distribution between dissolved and colloidal phases through reduction or oxidation. Under oxidizing conditions, nickel tends to bind to insoluble Fe and Mn (hydro)-oxides or dissolved organic matter, such as aromatic compounds.^{52,53} **Pb:** under the given concentrations, Pb is primarily present as Pb^{2+} . As the pH increases, it becomes less soluble and is found as PbOH^+ , $\text{Pb}(\text{OH})_2$, and $\text{Pb}(\text{OH})_3^-$. Compared with literature Pb removal rates in VSSF-CWs the removal in this study was considerably low, ranging from 28% to 41%. Mojiri *et al.* investigated the effectiveness of different constructed wetlands (CWs) in removing lead (Pb) from

wastewater. They found that a gravel-based CW achieved 47.5% Pb removal, while a wetland enhanced with biochar and zeolite achieved 99.9% removal with a HRT of 2.4 days.²⁴ Another study on modified CWs, which used biochar and iron scraps, showed a Pb removal rate of 98.6% at an HRT of 3 days.²⁰ These results suggest that a high HRT is important for the removal of Pb, which was significantly higher in the literature cited compared to this study. **Zn:** Zn removal was 89–96% in all wetlands with the highest removal in the combined approaches CW⁺ A and B (96% each). Interactions with Cr led to the precipitation as ZnCr_2O_4 which led to high removal even in the conventional CW. Another significant retention mechanism is the precipitation as carbonate under alkaline conditions induced by the limestone.^{54,55}



The HM removal potential of CW_{Zeolite} was lower than in the other modified wetlands. Given the fact that zeolite is a cation-exchanger, this process was minor to the physio- and chemisorption. The effectiveness of physio- and chemisorption is coupled to the specific surface area of the adsorbent, which is significantly higher in GAC than in zeolite. Furthermore, it is possible that other pollutants have saturated the zeolite, thereby inhibiting its ion-exchange capacity. Additionally, insufficient HRT may have also influenced the contact time with the zeolite which has a slower adsorption rate than activated carbon.⁵⁶

3.3. Comparative analysis of the removal of CW⁺ A, GAC and zeolite CW with the conventional benchmark approach

Another main purpose of this study was to compare the effectiveness of the modified adsorbent approaches with that of a conventional wetland to determine the removal potential of the different adsorbents in both single and combined adsorbent modes. Fig. 5 depicts the removal ratio of CW⁺ A and the two modified single adsorbent wetlands to CW_{Conventional}.

The data indicates that modifying facilitates the removal of a range of parameters in comparison to a conventional sand-based CW. Compared to the combined adsorbent wetlands CW⁺ A, CW_{Conventional} showed inferior removal of all pollutants. However, it exhibited superior removal of Cd in comparison to both CW_{GAC} and CW_{Zeolite}, as well as superior Cr removal in comparison to CW_{Zeolite}. Nevertheless, Cd ($0.41 \pm 0.60 \mu\text{g L}^{-1}$) and Cr ($0.86 \pm 1.43 \mu\text{g L}^{-1}$) were the HMs with the lowest concentrations, which significantly elevated the measurement error. In contrast with the anticipated outcome, the mean TOC removal was observed to be lower in the single GAC approach, with a ratio of 1.74 compared to 1.87 in CW⁺ A. This indicated that CW⁺ A was not approaching saturation, and that the combination of both adsorbents was exerting a synergistic effect on the removal of bulk organics. Considerably lower nitrification in CW_{Conventional} was observed with ratios of 7.10 (CW_{GAC}), 8.00 (CW_{Zeolite}) and 4.58 (CW⁺ A). This was caused by

higher retention times in the modified wetlands, induced by the water retaining biochar, as well as the enrichment of nitrifying bacteria in the more porous adsorbents. The high ratios of Cu removal ≥ 9.47 can be accounted to negative removal in 6 out of 15 analyses, indicating the leaching of Cu in the conventional CW. The removal of NH₄-N was similar in all wetland types. The combination of GAC and zeolite in CW⁺ A improved the removal of all selected parameters with the exception of Fe and PO₄-P. This slight decrease in PO₄-P removal compared to CW_{GAC} can be explained by the addition of zeolite, as it has almost no effect on the removal that can be inferred from similar removal ratios of CW_{Conventional} and CW_{Zeolite}. The efficiency of anion adsorption using natural zeolites is low due to the negative charge of the aluminosilicate structure.⁵⁷

3.4. Vertical removal behaviour

Sampling pipes in the different layers allowed to study the vertical removal behaviour as well as the contribution of each layer to the overall removal. The STP effluent/wetland influent concentration is represented at a filter depth of 0 m. DO content increased in the top layer of all wetlands compared to the effluent from the STP. The DO content remained stable throughout the filter depth, indicating adequate loading rates and sufficient resting times between feeding events (Fig. S1†). A study of Ye *et al.* observed a similar DO level rising in the wastewater in the top 10 cm by ratios up to 18–33 times.⁵⁸

TOC removal was significantly higher in the modified wetlands (74–94%) compared to the conventional wetland (53%) during the saturation events ($p < 0.01$). Especially the GAC-containing wetlands achieved average TOC effluent concentrations $\leq 1 \text{ mg L}^{-1}$ due to the high specific surface of GAC, which is consistent with previous studies (Fig. 6).⁵⁹ In comparison to upper layers, the bottom layers of CW_{GAC} (60%), CW⁺ A (71%) and CW⁺ B (72%) contributed the most to TOC removal. Vertical concentration distribution of TN showed a decrease in the upper (1–7%) and middle (18–30%)

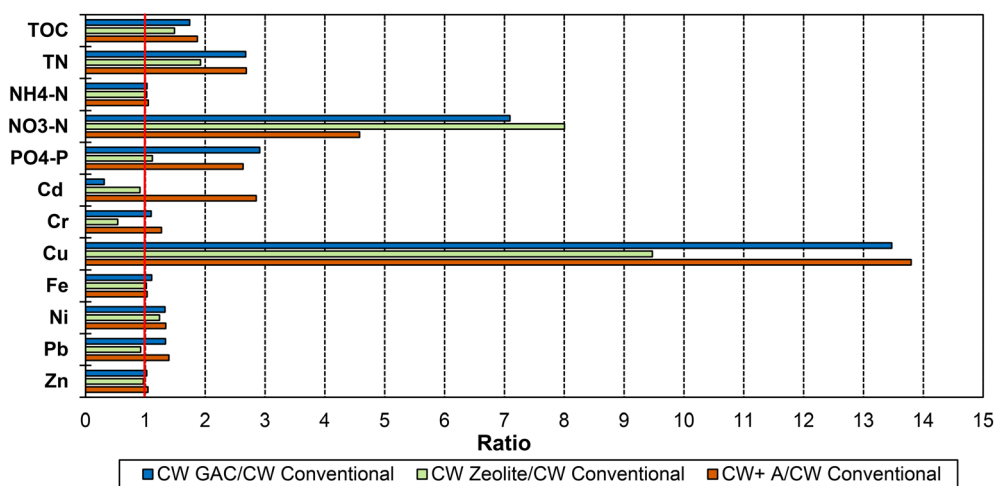


Fig. 5 Treatment efficiency expressed in ratio removal of CW_{Conventional} to CW_{GAC}, CW_{Zeolite} and CW⁺ A. Values < 1 indicate better removal in CW_{Conventional}, values > 1 better removal in the modified wetlands.



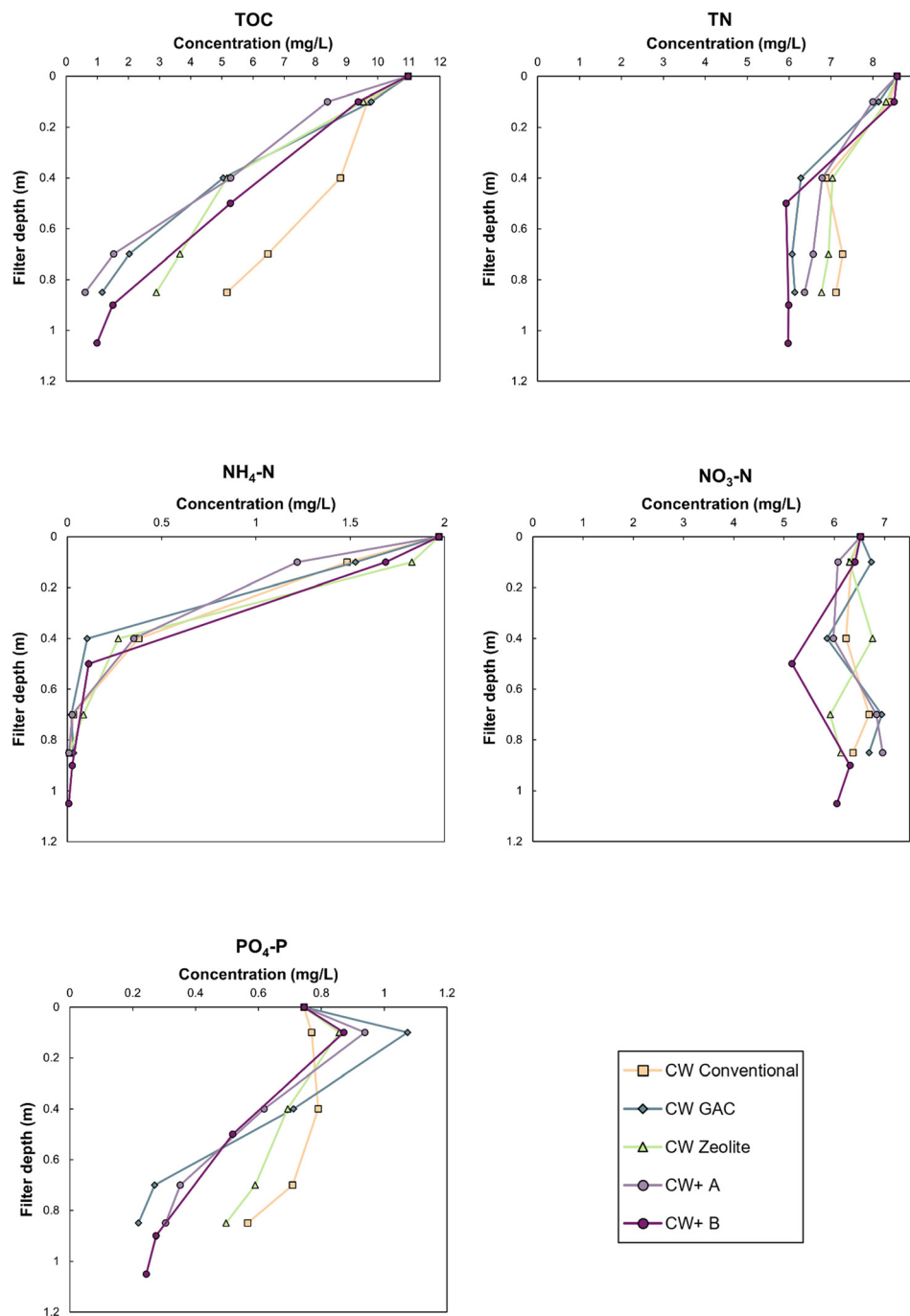


Fig. 6 Average vertical conventional wastewater parameter concentrations in the pilot wetlands during the saturation events.

layer of the wetlands with stagnating concentrations at the deeper sampling points. The main reason for this was rising $\text{NO}_3\text{-N}$ concentrations in the bottom layer except in $\text{CW}_{\text{Zeolite}}$ and to a minor degree in $\text{CW}_{\text{Conventional}}$. Microbial processes in the GAC containing layers resulted in higher $\text{NO}_3\text{-N}$ concentrations and negative removal than in the overlying layers with -19% , -14% , and -22% in CW_{GAC} , $\text{CW}^+ \text{A}$ and B respectively. The increase in EC in these layers was also associated with the presence of anionic $\text{NO}_3\text{-N}$, which was not subsequently denitrified.⁶⁰ Insufficient denitrification

was attributed to higher dissolved oxygen content, lack of organic carbon, and short retention time in the wetlands.

$\text{NH}_4\text{-N}$ removal in the upper layer was the highest in $\text{CW}^+ \text{A}$ (38%) followed by $\text{CW}_{\text{Conventional}}$ (25%). Lowest removal in the top layer was observed in the $\text{CW}_{\text{Zeolite}}$ (7%) which indicates no direct effect of the additive biochar. The majority of $\text{NH}_4\text{-N}$ was removed in the middle layer, accounting for 81–95% of the total removal, followed by a further total reduction of $\geq 98\%$ in the deeper layers of all wetlands indicating full nitrification. Although $\text{NH}_4\text{-N}$ effluent concentrations were lower in the



modified wetlands, the average effluent concentration of 0.01 mg L^{-1} in $\text{CW}_{\text{Conventional}}$ indicates that no enhanced adsorption additives were necessary. The increase of $\text{PO}_4\text{-P}$ concentrations in the upper layer of the wetlands containing biochar suggests that the biochar is leaching phosphate as this effect was not observed in the conventional wetland. While biochar has the potential to improve the availability of phosphorus in soils that have been amended with it, it can also lead to an increase in the release of phosphate from soil columns.^{61,62} However, the total average removal was higher in the modified approaches CW_{GAC} (71%), $\text{CW}_{\text{Zeolite}}$ (33%), $\text{CW}^+ \text{A}$ (59%) and $\text{CW}^+ \text{B}$ (62%) than in the conventional CW (24%).

The vertical HM concentration distribution is depicted in Fig. 7. Cd and Cr concentrations were considerably low in the WWTP effluent with $0.4 \text{ } \mu\text{g L}^{-1}$ and $0.6 \text{ } \mu\text{g L}^{-1}$ respectively. The biochar-containing top layers contributed to the removal of Cd, Cr, Cu, Fe and Pb when compared to the $\text{CW}_{\text{Conventional}}$ but showed no improvement on the removal of Ni and Zn. The upper layer exhibited the highest total removal for most HMs. This observation is consistent with other studies since most of the precipitation and subsequent filtration occurs in the top layer of CWs.⁶³ The modified wetlands showed overall superior removal of Cu and Ni compared to the conventional wetland.

In all wetlands, Cu is mostly removed from the top layer. The biochar top layers remove over 90% of Cu, while the sand top layer removes 82%. Cu primarily exists as insoluble CuO or in an exchangeable state, and has high bioavailability, which facilitates plant uptake.⁶⁴ However, plant-related processes like exhibited root bioaccumulation or phytostabilisation have limited direct contribution to retaining heavy metals.⁵ Ni and, to a lesser extent, Zn concentrations consistently decreased with increasing filter depth. This suggests that both HMs were at least partly available in soluble form. It is noticeable that in the modified wetlands, a re-release of Fe and Pb occurred in the middle sand layer. Based on the modelling, it can be inferred that Fe exists in the form of insoluble Fe(III) oxide within the pH range, while Pb tends to exist as poorly soluble PbOH^+ at a $\text{pH} > 5.9$. This suggests that these HMs were adsorbed in the biochar containing top layer with subsequent desorption and sedimentation, which led to higher concentrations in the underlying layer. However, Fe and, to a minor degree Pb, were removed in the underlying layers in all CWs. By evaluating the removal potential of the modified bottom layer, the removal was calculated in comparison to the concentration in the overlying layer. The modified layer in the combined approaches $\text{CW}^+ \text{A}$ and B removed 43% and 61% of Cd while the other CWs showed negative removal, especially in the bottom layer of $\text{CW}_{\text{Conventional}}$ with -87% . This may be due to the presence of soluble Cd^{2+} under the given pH range in the wetlands (see Fig. 4), as well as the relatively low concentrations of less than $0.4 \text{ } \mu\text{g L}^{-1}$. The modified bottom layers predominantly removed significantly more HMs except for Cr in the zeolite-containing wetland. Especially the combined adsorbent CWs enhanced the removal of Cd, Cr, Cu and Zn, CW_{GAC} had slightly better removal of Pb 69% compared to 61% in $\text{CW}^+ \text{A}$.

3.5. Effect of filter thickness on removal

To investigate the effect of the filter thickness, the removal rates of $\text{CW}^+ \text{A}$ (0.75 m) and $\text{CW}^+ \text{B}$ (0.95 m) were compared since they followed the same modification design (Fig. 8). No increase in TOC and $\text{NH}_4\text{-N}$ removal was observed in the deeper filter $\text{CW}^+ \text{B}$. The TN, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$ removal were positively influenced by the increased filter depth. These differences were significant ($p < 0.05$) between the TN removal of 38% in $\text{CW}^+ \text{A}$ and 55% in $\text{CW}^+ \text{B}$ and the $\text{NO}_3\text{-N}$ removal of 7% in $\text{CW}^+ \text{A}$ and 44% in $\text{CW}^+ \text{B}$ ($p < 0.01$).

The influence of the filter height on the HM removal efficiency appears to be negative for Cd, Cr and Pb. The average removal of Cd (31%) Cr (86%) and Pb (43%) in $\text{CW}^+ \text{A}$ is higher than in $\text{CW}^+ \text{B}$ (-0.35%), (76%) and (29%) respectively. This may be caused by the fact that Cd and Pb are present in their soluble forms under the given conditions and not as insoluble hydroxides (Fig. 4). Fe removal was slightly higher in $\text{CW}^+ \text{B}$ (87%) than in $\text{CW}^+ \text{A}$ (83%). The difference of 0.2 m in the filter layer does not seem to influence the removal of Cu, Ni and Zn. As these HMs have already been removed in the upper layers (Fig. 7), a thicker layer does not positively affect the removal. However, the thicker filter layer did not significantly influence the retention of all analysed HMs in the pilot wetlands. The similar removal of 0.75 m and 0.95 m filter thickness leads to the conclusion that the adsorbents in the smaller filter $\text{CW}^+ \text{A}$ have not yet reached saturation after 18 months of operation with a HLR of 144 L d^{-1} , resulting in an approximate treated wastewater volume of 80 m^3 .

3.6. Correlations

3.6.1. Influence of influent concentrations and filter depth. Positive, significant Pearson correlations were observed between the concentration of HMs in the influent and effluent except for Cu, Ni and Zn (Table S1†). Cd correlation was significant on a 2-tailed, 0.01 level in all wetlands. Which is coherent with the low removal rates of Cd in comparison to the other selected HMs. Second lowest removal was achieved for Pb which is also reflected by significant correlations in all wetlands ($p < 0.01$; $p < 0.05$ in CW_{GAC}). High influent concentrations of Cr influenced the effluent concentrations in $\text{CW}_{\text{Conventional}}$ and $\text{CW}_{\text{Zeolite}}$ significantly ($p < 0.01$). As this was not the case in the wetlands containing GAC, it can be concluded that GAC plays a crucial role in the removal of Cr.

NH_4^+ is another cationic contaminant commonly found in wastewater, alongside HMs. The simultaneous presence of HMs and NH_4^+ in wastewater leads to competitive adsorption mechanisms that alter the adsorption processes and cation exchange selectivity.⁶⁵ High $\text{NH}_4\text{-N}$ in the influent negatively affected the removal rates of Ni ($r = -0.47$; $p < 0.05$) and Pb ($r = -0.66$; $p < 0.05$) in CW_{GAC} and of Ni in $\text{CW}^+ \text{A}$ ($r = -0.41$; $p < 0.05$). The removal of Ni in $\text{CW}^+ \text{B}$ showed a similar ($r = -0.33$) but not significant trend ($p = 0.1$).



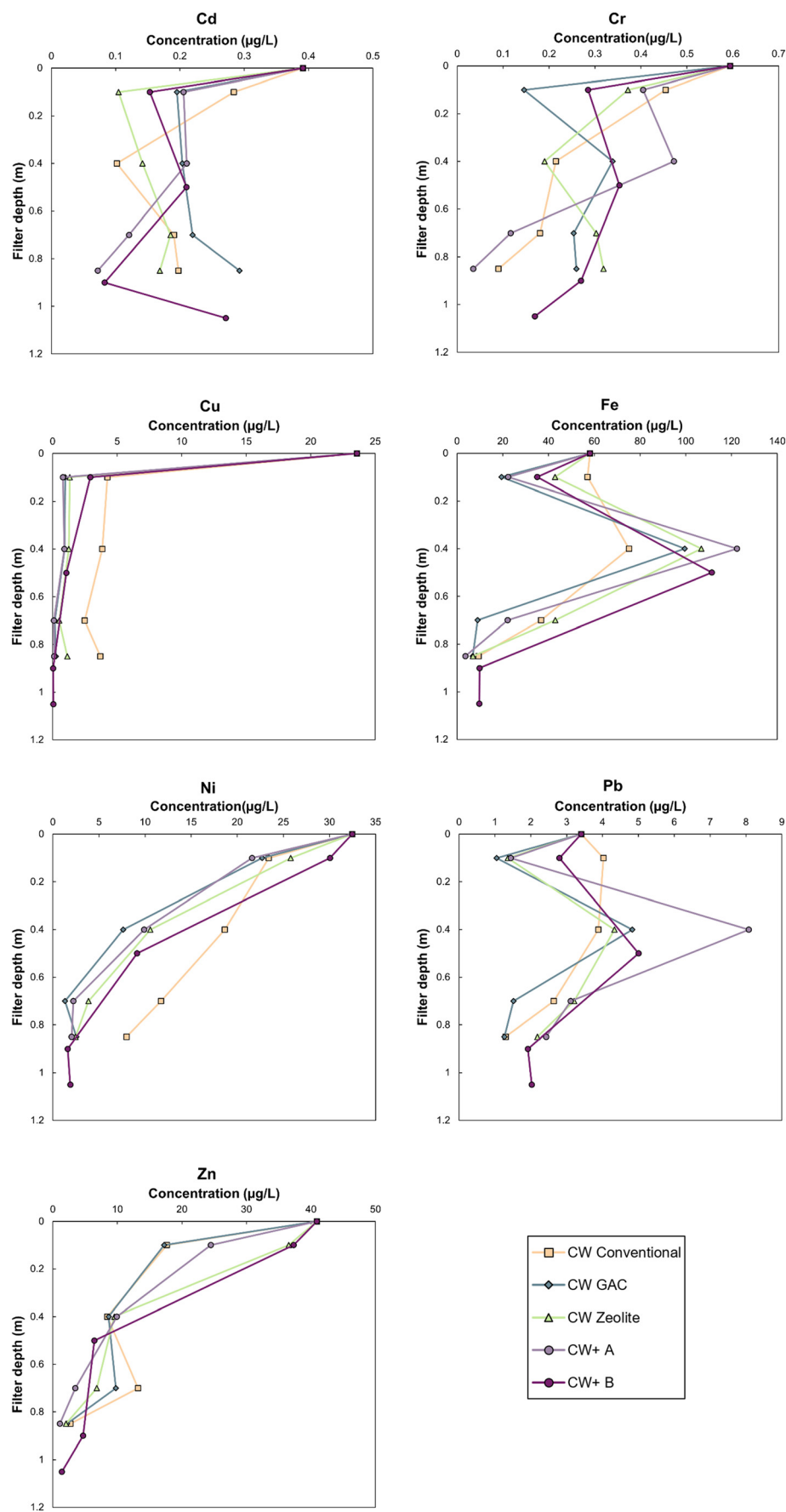


Fig. 7 Average vertical heavy metal concentrations in the pilot wetlands during the saturation events.



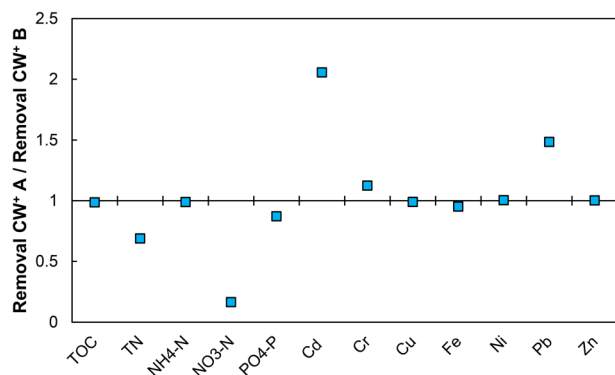


Fig. 8 Treatment efficiency of CW⁺ A and CW⁺ B expressed in ratio removal CW⁺ A to removal CW⁺ B. Values < 1 indicate better removal in CW⁺ B, values > 1 better removal in CW⁺ A.

Decreasing concentrations of Ni and Zn in particular were very strongly ($r \geq -0.94$) related to increasing filter depth, regardless of wetland type ($p < 0.01$), except for Zn where the effect was slightly lower in CW_{Conventional} and CW_{GAC} ($p < 0.05$) (Table S2†). Significant negative correlations of decreasing Cr concentrations with filter depth were observed in CW_{Conventional} ($p < 0.01$), CW⁺ A ($p < 0.01$) and B ($p < 0.05$). This trend was not observed in CW_{GAC} and CW_{Zeolite}, where concentrations stagnated or increased slightly in the deeper layers. In the conventional wetland, Pb concentrations decreased significantly with filter depth, indicating the need for a high filter thickness compared to the modified wetlands and the effect of the adsorbent additives in the retention of this HM.

3.6.2. Influence of environmental conditions. Since CWs are a nature-based technology, the removal of organic and inorganic compounds is influenced by the environmental conditions. The prevailing temperature especially affects (micro-) biological processes while HM speciation and coupled precipitation is highly influence by the pH. In addition, the solubility, mobility, and bioavailability of HMs are determined by their oxidation states. This emphasizes the significance of redox potential in their elimination.²⁷ The modified wetlands showed significantly lower effluent concentrations of Cd ($p < 0.05$) and lower Zn concentrations at higher temperatures. However, the effluent concentrations of Cu, Fe and Pb were not significantly influenced by temperature (Table S3†). Influent pH had the greatest effect on CW_{Zeolite}, whereas it had no effect on CW_{GAC}. Lower pH resulted in significantly lower effluent concentrations of Cd ($p < 0.05$), Cr, Fe, Ni and Zn ($p < 0.01$) (Table S4†). As a decrease in pH generally increases the solubility of metal ions, the ion-exchange properties positively influenced the retention of these HMs.⁶⁶ Significant positive correlations between HM removal and the redox potential were only observed for Ni but in all wetlands. Under oxidising conditions, Ni tends to co-precipitate with iron oxides due to their affinity for cations of similar size to Fe(II) and Fe(III).⁶⁷ This is also supported by the modelling results.

3.7. Assessment of the practical application potential

In a practical application scenario of an adsorbent modified CW, the maintenance and replacement of adsorbents, such as biochar, GAC zeolite, or other substrate materials used for pollutant removal become key operational parameters as adsorbent saturation is the main limiting factor. Replacement frequency will depend on the wastewater characteristic, quality of pretreatment, loading capacity, as well as loading rates and retention times. It is also crucial to tailor media type and adsorbent dosage to the local conditions in order to remain the cost-effective nature of CWs. High background DOC, solid matter and nutrient loads accelerate adsorbent saturation and can cause clogging, which emphasises the need for sufficient pre-treatment. Exchanging saturated adsorbents are a challenging procedure without disturbing the operation of the CWs. Once the material is saturated, modular media beds for staged replacement are an option to simplify the exchange of saturated material. Saturated GAC and zeolite can then be regenerated and reused. However, it is hard to predict the actual lifespan as it is highly case dependent. Actual pilot studies suggest that GAC in CWs can be used for at least 2–3 years of continuous treatment whereas biochar removal benefits start to diminish after approximately 1 year.^{59,68} It should also be noted that the lifespan of GAC is often extended through biofilm formation, resulting in biologically activated carbon (BAC), which increases its lifespan beyond that of purely physical adsorption.^{69,70} Incorporating biochar, GAC, and natural zeolite significantly improves the removal efficiency compared to conventional CWs. The increased costs of the adsorbents (350–1200 \$ per t for biochar, 800–3000 \$ per t for GAC and 30–120 \$ per t for natural zeolite) and the higher maintenance requirements are partly offset by the reduction in required surface area, depending on the land costs.^{29,30} Therefore, the low energy and personnel requirements, combined with the ecological compatibility of CWs, continue to make them highly suitable for decentralized wastewater treatment, particularly in rural or peri-urban areas where land is readily available and affordable.

4. Conclusion

Constructed wetlands have proven to be an effective polishing technology for treating wastewater effluent from WWTPs, with modifications using various adsorbents further enhancing their performance. This study demonstrated that incorporating materials such as zeolite, biochar, and GAC significantly improved the removal of organic and inorganic (trace) compounds, including HMs. While all modified CWs outperformed conventional systems in removing bulk organics, nutrients, and HMs, the combination of zeolite and GAC yielded the best results, leveraging multiple removal processes such as adsorption, ion-exchange, and complexation. The findings also highlighted the influence of factors like pH and retention time on HM removal, showing



that zeolite was particularly effective under lower pH conditions but required longer contact times due to slower adsorption kinetics and is more sensitive to elevated bulk organics and ammonium concentrations.

The research further indicated that, although increasing the filter depth enhanced NO₃-N and correlated TN removal due to extended retention times, it did not significantly impact the removal of other pollutants. Importantly, no saturation effects were observed, suggesting a longer operational lifespan and capacity for increased wastewater volumes. Modelling results pointed to co-/precipitation, sedimentation, and filtration as key mechanisms in HM removal under the studied wastewater characteristics. Overall, this study confirmed that CW modifications with adsorbents like zeolite and GAC provide high removal efficiency, even with shorter HRT, making them suitable for areas with limited space and offering cost-effective solutions for advanced wastewater treatment.

Future improvements could focus on the separation of the GAC and zeolite layers, optimising the system's overall efficiency to remove organics and HMs. It would be advantageous to position the GAC layer above the zeolite layer to remove bulk organics and promote nitrification, thereby protecting the more sensitive zeolite layer before targeting the removal of residual heavy metals. Given the effective removal observed at the current HLR, increasing the HLR is another potential area for future research to further reduce the space requirements of CWs.

Data availability

All required data supporting the findings are available in the manuscript and its ESI.† If the readers require any additional data, the authors will provide it in electronic format upon reasonable request.

Author contributions

L. O.: conceptualization, methodology, formal analysis, investigation, writing – original draft preparation, writing – review and editing; T. W.: validation, writing – review and editing, supervision; C. K.: conceptualization, methodology, validation, resources, writing – review and editing, supervision. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

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