Chapter 15 Performance Intensifications in a Hybrid Constructed Wetland Mesocosm

Adam Sochacki and Korneliusz Miksch

Abstract This chapter presents the study on the performance of a hybrid mesocosm constructed wetland system composed of two treatment step: vertical flow bed and floating emergent macrophyte unit (a tank with a vegetated floating mat). The objectives of this study were to assess the performance intensifications in this system by assessing the effect of: (i) combing two types of constructed wetlands, (ii) increasing saturation level in the vertical flow unit, (iii) applying artificial intermittent aeration in the vertical flow unit, on the removal of carbonaceous compounds, nitrogen species and (phosphate phosphorus) $P-PO_4$. The duration of the experiment was 378 days and it was divided into 4 periods: two periods with unsaturated vertical flow bed (but with different hydraulic loading rate values) and two periods with saturated bed of the vertical flow unit (in one period the bed was additionally intermittently aerated). The experimental system was fed with synthetic municipal waste water in a batch mode. It was observed that the intensification of the system's performance by integrating a vertical flow bed with partly saturated conditions and a floating emergent macrophyte unit ensured high removal efficiencies for total nitrogen (TN) and P-PO₄. Additionally, the application of artificial intermittent aeration in a vertical flow bed allowed achieving high removal efficiency of carbonaceous compounds (determined as dissolved organic carbon) without compromising the removal of TN and P-PO₄. The scope of further research will include optimization of the system for hydraulic retention time and batch duration and monitoring of the fate of selected micropollutants in the system.

Keywords Hybrid • Vertical flow • Constructed wetland • Floating emergent macrophyte • Intermittent aeration

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15.1 Introduction

The technology of treating municipal and domestic waste water in constructed wetlands (CWs) have rapidly developed over the last three decades (Wu et al. 2014) to become a viable alternative to energy intensive technologies for the sanitation of small communities (Garcia et al. 2010). Increasingly stringent water quality requirements in Europe necessitate further development of CWs and to intensify the treatment efficiency of these systems (Miksch et al. 2015) especially in terms of nitrogen and phosphorus removal (Wu et al. 2014). The intensification of the treatment processes in CWs can be achieved by various methods e.g. artificial aeration or integration of different types of CWs (Wu et al. 2014), the use of various filter media with high sorption capacity for the removal of phosphorus (Kim et al. 2015), or combination with other treatment technologies such as membrane bioreactors or advanced oxidation processes for the treatment of high-strength waste water and elimination of recalcitrant organics, respectively (Liu et al. 2015). The poor oxygen supply in conventional horizontal subsurface flow CWs or in the vertical flow CWs (VF-CWs) with saturated bed is a limiting factor for removal of organic matter and nitrogen (Boog et al. 2014; Wu et al. 2014). Aerated CWs are characterized by improved treatment efficiency, and therefore these intensified systems can have smaller footprint, and offer stable performance even in cold-climate countries and are less susceptible to clogging (Boog et al. 2014). Thus far, artificial aeration has been mostly introduced in the VF-CWs, however, other types of CWs have been also fitted with an aeration system. The artificial aeration in subsurface flow CWs can be operated continuously or in an intermittent pattern. The continuous aeration may lead to complete nitrification because anoxic conditions favourable for denitrification would not be provided. Thus, intermittent operation seems to be a viable solution for total nitrogen (TN) removal by providing alternate aerobic/anoxic conditions advantageous for simultaneous nitrification and denitrification and as a result enhancing overall nitrogen removal (Boog et al. 2014; Wu et al. 2014). Boog et al. (2014) observed improved removal of TN and nitrates and comparable removal of carbonaceous compounds in saturated VF-CWs with intermittent artificial aeration as compared with continuously aerated systems. Apart from the enhanced treatment efficiency, intermittently aerated CWs are more energy-economic than continuously aerated beds (Wu et al. 2014). There were various aeration patterns applied in the CW e.g. continuous and intermittent: 8 h on/4 h off (Boog et al. 2014), 1 h on/5 h off (Fan et al. 2013), or 5 min on/25 min off (Foladori et al. 2013). The removal of phosphorus in CWs is closely associated with the properties the filter material, because this element is mainly sorbed by or precipitated in filter media (Vohla et al. 2011). The conventionally applied filtered media as gravel or sand do not usually provide long-lasting elimination of phosphorus (Vohla et al. 2011). The poor elimination of nitrates and phosphorus in VF-CW (Kim et al. 2015) can be overcome also by combining this type of CWs with wetland systems promoting intensive nutrient removal such as, for example, free water surface CWs (FWS-CWs) (Vymazal 2005). These hybrid (or integrated) constructed wetlands combine different CW

units to optimize the treatment efficiency of the overall system (Fonder and Headley 2013) by complementing the advantages of each treatment unit (Vymazal 2013). It was reported that the application of FWS-CWs as the final treatment step not only improves nutrient removal but also the elimination of bacteria (Vymazal 2005), selected micropollutants (e.g. diclofenac) and microbial activity (Ávila et al. 2014). One of the variants of the FWS-CWs is a floating emergent macrophyte CW (FEM-CW), frequently also termed as floating treatment wetland, in which emergent macrophytes grow on a buoyant artificial mat or raft floating on a surface of a pond (Fonder and Headley 2013). Plant roots grow through the porous mat and hang into the water column (Borne et al. 2014), which provides extensive area for the growth of biofilm and entrapment of fine suspended particulates (Tanner and Headley 2011). As the plants are not rooted, they are forced to acquire the nutrients directly from the water, which may lead to significant improvement in the rate of nutrient uptake rate by plants (Tanner and Headley 2011). The important feature of FEM-CWs is that their buoyancy enables to tolerate wide fluctuations in water depth (Tanner and Headley 2011).

The objectives of this study were to assess the performance intensifications in a mesocosm CW system by assessing the effect of: (i) combing two types of CWs, namely VF-CW and FEM-CW, (ii) increasing saturation level in the VF-CW, (iii) applying artificial intermittent aeration in the VF-CW, on the removal of carbonaceous compounds, nitrogen species and (phosphate phosphorus) P-PO₄.

15.2 Methods and Materials

15.2.1 Experimental System

The experimental system was a mesocosm hybrid CW comprising two treatment step: vertical flow (VF-CW) bed and a tank with a floating island, which will hereafter referred to as a floating emergent macrophyte constructed wetland (FEM-CW) according to the nomenclature proposed by Fonder and Headley (2013).

The VF-CW was constructed using plastic cylindrical tank (diameter 60 cm, height 90 cm), which was filled up to 80 cm with mineral media (15 cm of 4–8 mm gravel at the bottom, and 65 cm of 0.5–1.0 mm quartz sand; both fraction were separated using polyester mesh). The filter media were approved for potable water sand filters and were purchased from Ecopol Sp. z o.o. (Police, Poland). The VF-CW tank had four orifices (diametrically opposite) on the side wall at the bottom. Three orifices were interconnected with a plastic pipe that extended up to the upper brim of the barrel, which was used a passive aeration system until day 350 of the experiment and further on it was connected with an air pump through plastic tubing. The fourth orifice was used as an outflow of the treated waste water. Additionally there were four more outlets situated every 5 cm above the bottom outlet, but they were not used in this experiment. No specific air distribution system, as e.g. perforated

pipes, was used inside the VF-CW assuming that the bottom layer of gravel would distribute the air sucked or pumped into the system evenly. The bed of VF-CW was inoculated using return sludge at the beginning of the experiment. This sludge originated from municipal waste water treatment plants using conventional activated sludge technology. The mixed liquor suspended solids concertation in the sludge was 5 g/L and the volume of the sludge used to inoculate the system was 20 L.

The tank of the FEM-CW was constructed using steel frame and glass panes (length 150 cm, width 100 cm, depth 50 cm). The artificial floating island (120 cm length, 80 cm width and approx. 10 cm thickness) was a buoyant structure made of lime-wood frame with a willow wicker weaving supporting 10-cm layer of light expanded lay aggregates covered with a plastic net. The artificial floating island was purchased from Ogrody Wodne (Gorzycko Stare, Poland). In order to maintain initial buoyancy of the floating island a rectangular frame (120 cm length, 80 cm width, with an additional transversal pipe) made of drainage pipes filled with empty PET bottles (11 bottles in total) was placed beneath the island after a year of the experiment. The water depth in the FEM-CW was 45 cm and was increased to 50 cm on day 329 for aesthetic reasons, which corresponded to active volume 675 L and 750 L, respectively. The VF-CW and FEM-CW were connected by a stainless steel braided rubber hose. The inlet of the waste water in the FEM-CW was situated in the corner of the tank approx. 5 cm above the bottom, and the outlet was situated in the diagonally opposite corner of the tank also approx. 5 cm above the bottom. Prior to the start-up the FEM-CW tank was filled with the effluent of microcosm VF-CWs treating the same synthetic waste water.

The experimental system was operated under indoor conditions with artificial lighting system comprising one 600 W high-pressure sodium lamp (HPS) and one metal-halide lamp (600 W), of which the former was hung above the FEM-CW, and the latter was put on a post in an inclined position adjacent to the VF-CW (Fig. 15.1). Before day 262 only one lamp was used (600 W HPS), however due to increasing shading of the FEM-CW by the vegetation in the VF-CW another lamp was added to the lighting system. The lighting system was purchased from Flora and Fauna Sp. z o.o. (Poland). The light/dark conditions were 16/8 h throughout the experiment.

The FEM-CW tank was aerated continuously using an air pump Tetratec APS-150 (3.1 W, with a maximum airflow of 2.5 L/min) connected with a ceramic stone diffuser placed on the bottom of the tank. The aeration in the FEM-CW was used to prevent oxygen depletion and to induce mixing. The floating island occupied significant area of the tank (64%) and it would obstruct oxygen diffusion into the system leading to aesthetically displeasing appearance of the system, which was noticed in the week preceding the start-up of the system. On day 351 the use of the Tetratec air pump was discontinued and it was replaced with an air pump HIBLOW-HP-60 manufactured by Techno Takatsuki (Japan) with a maximum airflow 60 L/min. The HIBLOW-HP-60 air pump was used to aerate both the VF-CW and FEM-CW units in the aeration pattern 4 h on/2 h off. Also the ceramic stone diffuser was replaced by an EPDM-HD200 disc diffuser (effective diameter 184 mm) manufactured by Jäger Gummi und Kunststoff GmbH (Germany) mounted on a concrete base and placed on the bottom of the FEM-CW tank.



Fig. 15.1 Experimental mesocosm system: VF-CW (*left*) and FEM-CW (*right*), photo taken on day 342 of the experiment

The VF-CW was planted with 10 rhizomes of common reed (Phragmites australis) but it was observed that this plant desiccated completely, probably due to insufficient substrate moisture, which was related to the mode of operation (Table 15.1). For this reason, common reed was completely removed from the system and replaced with 5 seedlings (in 2-L pots) of giant miscanthus (Miscanthus × giganteus) on day 65 of the experiment. It should be noted that the bed of VF-CW was not saturated with water prior to the start-up of the system, which probably prevented establishment of common reed. The floating island used in the FEM-CW was initially planted with 24 seedlings of sweet flag (Acorus calamus), 3 seedling of yellow flag (Iris pseudacorus), 2 seedlings of soft rush (Juncus effusus) and 2 seedlings of dwarf scouring rush (Equisetum scirpoides). American frogbit (Limnobium spongia) was added as a free-floating plant and common duckweed (Lemna minor) appeared spontaneously in the FEM-CW. Three seedlings of parrot feather (Myriophyllum aquaticum) were planted on the bottom of the tank in 100-mL plastic containers filled with sand. Other plants that were successfully planted on the floating island in the further part of the experiment were: purple loosestrife (Lythrum salicaria), yellow monkey-flower (Mimulus luteus), water mint (Mentha aquatica), bulrush Scirpus (Schoenoplectus) lacustris, bog bulrush (Schoenoplectus mucronatus), brooklime (Veronica beccabunga), watercress (Nasturtium officinale), creeping jenny (Lysimachia nummularia), great willowherb (Epilobium hirsutum).

Table 15.1 O	JEI AUIOII CIIAI L	•							
							COD	VF-CW	
		Number of			Operation	HLR,	load,	aeration,	HRT
Period	Days	batches	Feeding/resting, d	Bed saturation	mode	$mm \ d^{-1}$	$g m^{-2} d^{-1}$	pattern	(FEM-CW), d
A	1-50	34	5/2	Unsaturated	Batch	32	26	No	81
B	51-251	144	5/2			64	24	No	88
Transitory	252-293	Various setting	s						
C	294-350	18	2/5	Partially saturated	Batch	80	63	No	157
D	351–378	4	1/6		Batch	213	198	Yes, 4 h	175
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Table 15.1

The plants that were planted on the island but failed to adapt to its specific conditions were: graceful cattail (*Typha laxmanii*), duck potato (*Saggitaria latifolia*), Japanese sweet flag (*Acorus gramineus*). It was observed that yellow flag had the highest growth rate and greatest biomass production.

The experimental system was fed with simulated municipal waste water prepared according to the protocol by Nopens et al. (2001) with several adjustments (doubled dose of the compounds with the exception of Cr, Cu, Mn, Ni, Pb, Zn, Mg, Fe salts; also soy oil and starch were not used. The influent was prepared in tap water by dissolving the following components (Nowrotek et al. (2016)): urea (208.76 mg/L), NH₄Cl (62.4 mg/L), yeast extract (264 mg/L), skim milk powder (118 mg/L), sodium acetate (510.4 mg/L), peptone (40 mg/L), KH₂PO₄ (41.37 mg/L), KCr(SO₄)₂·12H₂O (0.96 mg/L), CuSO₄·5H₂O (0.781 mg/L), MnSO₄·H₂O (0.108 mg/L), NiSO₄·7H₂O (0.359 mg/L), PbCl₂ (0.1 mg/L), ZnCl₂(0.208 mg/L), MgSO₄·7H₂O (4.408 mg/L), FeSO₄·7H₂O (11.6 mg/L). In period B of the experiment (Table 15.1) the influent was diluted 1:2 using tap water to increase the hydraulic loading rate (HLR) in this period.

The experiment presented in this chapter was started on the 15 October 2014 and the presented data refer to 378-day operation, this is until the 26 October 2015. The operation of the experimental system can be divided into four distinctive periods A-D (Table 15.1) based on the operation parameters. In periods A and B the VF-CW unit was operated as an unsaturated bed and two HLR values were applied. In periods C and D the VF-CW was partially saturated and it was additionally intermittently aerated in period D. In the transitory the bed saturation level was gradually increased in every batch up to the level of 48 cm (maintained in period C), but the waste water samples were not taken. It should be noted that the operation of the system was divided based on the values of the parameters that can be controlled or monitored, therefore the shift from common reed to giant miscanthus in the VF-CW was not considered as an onset of a new period, however the conditions created by the development of the rhizosphere of this plant should not be neglected. The presented values of the hydraulic retention time (HRT) in the FEM-CW (Table 15.1).

In all the periods the VF-CW step was fed in batch mode with various feeding/ resting patterns and with the entire cycle being invariably 7 days long. In periods A and B the VF-CW was fed for 5 days (Monday-Friday) and then rested for 2 days (Saturday and Sunday) and was operated in a free draining mode. In periods D and C the bed was fed either for 1 or 2 days (Monday or Monday and Tuesday, respectively) and was rested for 6 or 5 days, respectively. In contrast to period A and B, in periods C and D the bed was partially saturated during the resting period. Based on the bed porosity of 33% it was calculated that the water saturation level in the VF-CW was 48 cm (60% of the bed volume) and 64 cm (80% of the bed volume) in periods C and D, respectively.

The bed was fed manually using a pitcher and the entire daily batch was introduced over a short time of approx. 10 min. The HLR was increased in period B by diluting the waste water in order to reduce HRT in the FEM-CW. However, it can be seen in Table 15.1 that HRT in fact slightly increased due to significant water loss due to rapid growth of giant miscanthus in the VF-CW.

15.2.2 Sampling Procedure

The effluent from the VF-CW was collected by draining the entire batch into a container from which the sample was taken. Then the remaining volume was fed into the FEM-CW tank. The samples of the waste water treated in the FEM-CW unit were taken by withdrawing 1 L of the waste water by opening the outlet valve. All the samples were filtered using qualitative filter paper (MN 615 filter for medium fast filtration from Macherey-Nagel GmbH & Co. KG, Germany) prior to analysis.

15.2.3 Wastewater Analysis

 $N-NH_4$ was analysed photometrically using 1.00683.0001 Spectroquant Ammonium Test from Merck KGaA (Germany). COD was determined photometrically using 1.14540.0001 and 1.14691.0001 Spectroquant COD Test from Merck KGaA (Germany). Two measuring ranges were applied - 100–1500 mg/L and 10–150 mg/L. DOC concentration was determined by TOC analyser Shimadzu TOC–L. DOC was analysed using the non-purgeable organic carbon method. DOC was not analysed in period A of the experiment.

Manganese (II) ions were determined using 1.4770.0001 Spectroquant manganese test from Merck KGaA (Germany). The Mn^{2+} concentration was measured only in periods C and D. Oxidized nitrogen forms concentration was presented as a sum of N-NO₃ and N-NO₂, because N-NO₂ was found at very low concentrations almost throughout the entire experiment with the exception of period A of the experiment. N-NO₃ was analysed photometrically using 1.09713.0001 Spectroquant nitrate test from Merck KGaA (Germany). N-NO₂ was analysed using 1.4776.0001 Spectroquant nitrite test from Merck KGaA (Germany). P-PO₄ was analysed photometrically using 1.00798.0001 Spectroquant.

The oxidation-reduction potential (ORP) value was measured using an ORP HI98201 m from the Hanna Instruments (USA). This parameter was measured in the effluents from the VF-CW and FEM-CW. The ORP was measured only in periods C and D. pH was measured using an electrode connected to a pH-meter WTW 330.

Sulphate concentration was determined using 1.14548.0001 Spectroquant sulphate cell test purchased from Merck KGaA (Germany). From day 358 of the experiment sulphate was determined using 1.14791.0001 Spectroquant sulphate test from Merck KGaA (Germany). The sulphate concentration was measured only in period C and D. Total nitrogen (TN) concentration was calculated as a sum of TKN (total Kjeldahl nitrogen, results are not presented in this paper), N-NO₃ and N-NO₂ (nitrite nitrogen) in both the influents and the effluents. TKN was determined using the Kjeltec System from Foss Tecator according to the method reported in Nowrotek et al. (2016). Due to servicing, the Kjeltec apparatus was not used in days 228–350

and the cuvette TN test 1.14763.0001 (Spectroquant nitrogen (total) cell test purchased from Merck KGaA, Germany) was used instead.

The inflow and outflow water volumes for the VF-CW were measured by graduated pitcher with an accuracy of ± 0.1 L. The outflow water volume for the FEM-CW corresponded to the volume that was had to be withdrawn to maintain constant water depth in the tank.

15.2.4 Statistical Analysis

The Shapiro-Wilk W test was employed to test for normality of the data. Most of the subsets of the performance data had non-normal distribution, therefore median and the median absolute deviation (MAD) were used as descriptors of the central tendency and dispersion of data distributions. Normally distributed data sets (as independent groups) were compared by the use of Student's *t*-test and non-normally distributed data sets (as independent groups) were considered statistically significant if p < 0.05. Statistical testing was performed using the STATISTICA 10 software (StatSoft, Inc. 2011).

15.3 Results and Discussion

The efficiency of the treatment in terms of standard waste water quality parameters is listed in Table 15.2. Additionally, water loss as a measure of evapotranspiration is given. All the removal efficiency values (except for pH and water loss) were calculated for the VF-CW (influent against VF-CW effluent), for the FEM-CW (VF-CW effluent against the FEM-CW effluent) and for the entire system (influent against FEM-CW effluent).

It can be seen that the removal of organic matter determined as COD in the VF-CW was affected by the shift from the unsaturated to saturated conditions, which is due to the fact that the rate of biodegradation processes is lower under anoxic conditions (Kadlec and Wallace 2009). The high COD concentration in the FEM-CW effluent in period D could have been affected by high COD values in period C, which were reflected in the quality of the FEM-CW effluent with a time shift due to very low dilution rate. The other reason might be that the installation of a new air pump and a new diffuser on day 350 with much higher air flow resuspended the bottom sediments, which as a result increased the concentration of organic matter in the waste water. It should be also noted that this high value of COD might be an artefact as two different values (80 and 246 mg/L on average) were obtained during the measurements depending on the measuring range. Based on the value of the absorbance it was decided that the higher value was more trustworthy (for the lower COD value the absorbance was>1). In the other periods, this was not a case,

			VF-CW efflu	ient	FEM-CW effluent		
Parameter	Period	Influent	Conc.	RE [%]	Conc.	RE [%]	Total RE [%]
COD	$\Delta n=4$	815+3	138 + 30	83+4	25+4	77+4	97+0
COD	B_{n-5}	380+174	63+34	81+5	43 ± 10	13 ± 19	86+2
	C n-3	783+35	526+126	30+4	57 ± 20	91+2	94+2
	$D_{n=4}$	030 ± 40	320+20	50±4 63+4	238+23	31 ± 24	75+10
DOC	Δ n=0	950±49	320129	0514	230123	51124	75±10
DOC	$R_{n=10}$	-	13 2+5 0	02+3	125+17	-	02+1
	D, n = 10	104.2 ± 10.0	15.2 ± 5.0	92±3	12.3 ± 1.7 165+02	11±30	92±1
	C, II=3	333.3 ± 00.1	139.4±91.4	40±33	17.2 + 0.0	90±0	95±1
	D, n=4	$3/2.1 \pm 3.0$	23.8±9.8	93±3	17.5±0.9	21±29	95±0
$N-NH_4$	A, n=4	123.5±18.5	39.0±12.5	69±10	7.5±2.5	80±4	91±16
	B, n=4	25.0±7.0	6.0±1.0	76±5	3.0±1.0	50±17	92±4
	C, n=4	60.3 ± 24.3	43.0 ± 4.8	37±29	6.3±1.8	83±7	90±7
	D, n=4	23.0 ± 2.0	17.2±5.9	30±21	7.1±1.6	57±6	74±2
$N-NO_2+N-NO_3$	A, n=4	2.7±0.7	75.0±19.0	-3440 ± 1347	37.1±3.9	45±16	-1255 ± 156
	B, n=7	2.8 ± 0.6	58.5 ± 12.3	-2286 ± 505	38.1 ± 5.0	40 ± 12	-1168 ± 290
	C, n=3	1.7 ± 0.7	4.2 ± 0.7	-54 ± 95	7.0 ± 3.5	-45 ± 61	-577 ± 370
	D, n=4	2.3 ± 0.3	11.3 ± 3.8	-327 ± 62	1.7±0.6	83±5	40±8
TN	A, n=4	158±5	113±9	16±5	38±5	71±4	76±6
	B, n=5	79±14	72±6	2±6	37±3	49±3	53±12
	C, n=3	220 ± 20	44±1	76±3	12±2	77±1	94±1
	D, n=4	155±7	32±4	81±2	14±4	57±4	93±1
P-PO ₄	A, n=4	34.8 ± 0.8	28.1±4.3	29±5	13.2±1.1	51±4	64±2
	B, n=8	13.1±4.2	12.8±3.8	15±10	8.2±1.8	29±8	38±13
	C, n=3	33.0±12.9	7.6±0.4	64±8	8.2±1.9	-14 ± 6	59±12
	D, n=4	24.1±1.8	8.2±2.2	66±7	5.6±1.1	30±17	74±7
pН	A, n=4	7.29±0.12	7.16±0.46		7.44 ± 0.08		
	B, n=9	7.93 ± 0.20	8.10±0.18		8.45 ± 0.16		
	C, n=3	7.99 ± 0.26	7.84±0.22		8.29 ± 0.19		
	D, n=4	7.93±0.12	8.41±0.12		8.81 ± 0.05		
Water loss	A, n=3	11.0±0.0 L	12.2±2.0 L	-9±20			
	B, n=2	18.0±0.0 L	10.6±2.9 L	41±16			
	C, n=7	45.0±0.0 L	13.4±5.3 L	70±12			
	D, n=4	60.0±0.0 L	29.5±1.5 L	51±3			

Table 15.2 Influent and effluent concentrations (mg/L; median \pm MAD) and removal efficiencies (RE; %; median \pm MAD) of the standard waste water parameters for all the treatment steps, and influent and effluent water volumes, and water loss (L, median \pm MAD) for the VF-CW

because only one measuring range was valid. The COD analysis could have been interfered by the presence of ferrous iron, heterocyclic compounds or readily volatile hydrocarbons, which could have been present in the effluent from the VF-CW and FEM-CW because of the reducing conditions, presence of plant exudates or specific by-products of microbial degradation (Merck 2013). It is therefore more meaningful to characterize the removal of organic matter using DOC. It can be seen that the VF-CW displayed very high removal of DOC (>90%) when the bed was operated in an unsaturated mode (period B) and when the bed was artificially aerated (period D). However, in the period C when the VF-CW was operated in a saturated mode without aeration the removal was markedly lower than in period B (at p < 0.05), which was due to the fact that organic matter degradation rate is lower under anoxic conditions. The effluent concentration of DOC in the FEM-CW was invariably below 20 mg/L, which corresponded to very high overall removal efficiency (>92%).

The removal efficiency of N-NH₄ appears to be affected by the bed saturation as the removal in periods A and B when the bed was operated in an unsaturated mode is approx. 70% (no statistically significant differences) and in periods C and D when the bed was partially saturated the removal was approx. two-fold lower. The shift from unsaturated to saturated conditions in the VF-CW decreased the nitrification efficiency, but the increased amount of N-NH₄ could have been also a result of dissimilatory nitrate reduction to ammonium, which was determined as an important pathway contributing to nitrate removal in CWs (Zhi et al. 2015). The combined concentration of the oxidized N species (N-NO₂ and N-NO₃) in the effluent from the VF-CW was clearly dependent on the bed saturation. In periods A and B when denitrification was not favoured by bed saturation the concentration of N-NO₂ and N-NO₃ was above 50 mg/L (removal efficiency -3440% and -2286%, respectively) and in periods C and D when the bed was partially saturated the concentration of oxidized N species was approx. 10 mg/L or lower (removal efficiency -54 % and -327%, respectively). The concentration of N-NO₂ and N-NO₃ in the FEM-CW effluent was decreasing in the course of the experiment, which corresponded to the concertation in the VF-CW effluent. In period D the concentration of the oxidized N species in the influent and effluent of the whole system was almost equal and at very low level of approx. 2 mg/L.

Similarly, the saturated conditions favoured TN removal by the putative pathways of denitrification and dissimilatory reduction of nitrate to ammonium, which was noticed in period C and D, during which the TN removal efficiency was 76% and 81%, respectively. Noteworthy, these differences were not statistically significant. In contrast, the removal of TN was very low or negligible in periods A and B, when the VF-CW was operated in an unsaturated mode. For the TN removal, statistically significant differences were observed between saturated and unsaturated periods in any combination (period A and C, A and D, B and C, B and D). In any period the FEM-CW provided additional removal of TN in the range of 49-77%. The overall maximum removal efficiency for TN was achieved in periods C and D and was $\geq 93\%$.

The performance of the presented hybrid system for P-PO₄ was in the range from 38 to 74%, which is in the range reported in the review by Vymazal (2013) for various hybrid systems combining subsurface flow CWs with free water surface systems. It can be clearly seen that under saturated conditions the removal of P-PO₄ was increased as compared to unsaturated conditions from 15–29% to 64–66%. Interestingly, partially flooded bed and the corresponding reducing conditions in period C (Table 15.3) did not trigger phosphorus release due to solubilisation of iron

			VF-CW		FEM-CW		
Parameter	Period	Influent	Conc. [mg/L]	RE [%]	Conc. [mg/L]	RE [%]	Total RE [%]
SO4 ²⁻	C, n=2	102±6	213 ± 102	-104 ± 88	182±24	-4±39	-77 ± 13
	D, n=4	99±13	241±63	-75±75	210±35	9±10	-76±19
Mn ²⁺	C, n=2	$<0.50\pm0.00$	10.35 ± 8.25	-1970 ± 1650	$<0.50\pm0.00$	87 ± 11	0 ± 0
	D, n=4	$<0.50\pm0.00$	0.64 ± 0.14	-27 ± 64	$<0.50\pm0.00$	18 ± 18	0 ± 10
ORP, mV	C, n=4		-162 ± 10		50 ± 28		
	D, n=4		75±14		57±5		

Table 15.3 Influent and effluent concentrations (mg/L; median \pm MAD) and removal efficiencies (RE; %; median \pm MAD) of sulphates, manganese (II) ions, and ORP (mV)

minerals and associated phosphorus co-precipitates (Kadlec and Wallace 2009). On the contrary, despite low ORP values (Table 15.3) the P-PO₄ release or decrease of its removal efficiency was not observed as e.g. in the study of Kim et al. (2015), in which the removal P-PO₄ was decreased with increasing saturation level and was released in completely flooded VF-CW system. The duration of the partly and fully saturated phase in the study of Kim et al. (2015) was comparable and also the saturation level was similar: 30 cm - 70 cm (fully flooded) in Kim et al. (2015) and 40 cm (period C) and 64 cm (period D) in the present study. The results obtained in this study may suggest that the enhanced removal efficiency of P-PO₄ was due to increased saturation and the extended retention time, which was 1 week, which in turn probably stimulated plant uptake of P-PO₄. The removal of P-PO₄ in the FEM-CW was less pronounced than in the VF-CW during periods C and D. This is probably due slower development of the plant biomass in the FEM-CW as compared to rapid and riotous growth of miscanthus in the VF-CW. It should be mentioned that, however, the FEM-CW provided additional removal of $P-PO_4$ in the range of 29-51%, with the exception of period C. In order to better illustrate the contribution of the VF-CW and FEM-CW to the removal of TN and P-PO₄ relative removal efficiency was calculated as the proportion of the concertation removed in a single step to the overall concentration removed (Fig. 15.2). The onset of the saturated conditions in the VF-CW significantly shifted the balance between the contribution of the treatment units as the sinks for TN and P-PO₄. For both contaminants, the contribution of the VF-CW to their removal was low in periods A and B, however, after the onset of the saturated conditions in the VF-CW this subsystem played the predominant role as the sink of TN and P-PO₄.

The differences between the pH value in the influent and VF-CW effluent were not statistically significant with the exception of period D when the pH value increased by 0.5 during the treatment, which can be attributed to the alkalinity production in the denitrification process (alkalinity was not measured). The increase of the pH value observed in the FEM-CW in the course of the experiment can be attributed to CO_2 consumption by the phytoplankton. The water loss value due to evapotranspiration increased from slightly negative value in period A to 41 % in period B, which should be attributed to the rapid growth of miscanthus that was planted during



Fig. 15.2 Relative contributions of the treatment units to the overall removal efficiency for TN (*left*) and P-PO₄ (*right*)

this period. In periods C and D it further increased to 70 and 51 %, respectively, due to continuous development of vegetation and also increased contact between the rhizospehere and the treated waste water due to the operation mode. The observed higher water loss in period C (August and September) than in period D (October) was probably due to higher ambient temperature associated with the seasonal changes. Comparing the results presented in Table 15.2 with the performance data of hybrid constructed wetlands with FWS step collected and elaborated by Vymazal (2013) it was observed that the performance of the presented hybrid system was especially high in terms of TN and P-PO₄ (TP was reported by Vymazal 2013) removal, which was higher than the results for 86% of the systems (6 out of 7) presented in Vymazal (2013). The performance of the system discussed in this chapter for other parameters was in the middle of the range. This comparison was made using the data for period D.

Apart from the parameters routinely measured to characterize the quality of treated waste water additional parameters that reflect oxidation-reduction conditions were determined. These parameters were the concentration of SO_4^{2-} and Mn^{2+} and also the value of ORP and were determined only in periods C and D (Table 15.3), this is before and after the VF-CW aeration was introduced.

As can be seen from Table 15.3, partial flooding of the bed in the VF-CW did not stimulate sulphate reduction, despite ORP values typically occurring in sulphate reduction zone (Reddy and DeLaune 2008), but triggered Mn^{2+} release, because Mn(IV) is an electron acceptor with higher reduction potential than SO_4^{2-} . The observed release of SO_4^{2-} in period C and D cannot be elucidated without additional analysis, but it can be hypothesized that it was related to desorption of this anion or rewetting of the filtration material that was not subjected to prolonged contact with waste water percolating through the bed in periods A and B (Whitfield et al. 2010). It seems less likely that the sulphate release was caused by reoxidation of sulphides present in the VF-CW, because this system was operated in a mode preventing sulphate reduction to sulphides. The aeration of the VF-CW increased the ORP value of the effluent by more than 200 mV, which also translated to much less pronounced Mn^{2+} release.

The removal rates and percentage mass removal values are given in Table 15.4 for the VF-CW and the entire system. The removal rates for the entire system are generally lower than for the other hybrid CWs including FWS stage discussed in the

		VF-CW		VF-CW and FEM-CW		
Parameter	Period	Loading rate VF-CW, g m ⁻² d ⁻¹	Removal rate VF-CW, $g m^{-2} d^{-1}$	Percentage mass removal, %	Removal rate VF-CW, g m ⁻² d ⁻¹	Percentage mass removal, %
COD	В	48.4	46.0	95.1	53.0	96.7
	D	27.5	22.5	81.8	3.77	84.5
DOC	В	20.9	20.4	97.6	3.2	97.7
	D	11.3	10.9	96.4	1.7	97.6
TN	В	10.0	7.4	73.2	1.4	86.2
	D	4.7	4.2	89.2	0.7	95.5
N-NH ₄	В	3.2	3.0	92.9	0.49	96.5
	D	0.7	0.4	61.5	0.1	84.1
$P-PO_4$	В	1.7	1.2	71.2	0.2	81.7
	D	0.7	0.6	82.3	0.1	88.1

Table 15.4 Treatment performance data in periods B and D of the system operation

review of Vymazal (2013). This is due to the fact that the presented system was not optimized in terms of the HRT value in the FEM-CW and the batch duration in the VF-CW, which were both relatively long compared to commonly applied values. The percentage mass removal values in the VF-CW were compared with the results obtained by Boog et al. (2014) for intermittently (8 h on/4 h off) aerated unplanted VF-CWs. It was observed that the values percentage mass removal were higher in both periods (Table 15.4) for DOC (TOC was reported in Boog et al. 2014), in period D for TN, and in period B for N-NH₄. The percentage mass removal reported by Boog et al. (2014) for these parameters was 92.2, 78.0 and 89.2 %, respectively.

Based on the population equivalent (pe) 80 g COD/pe (Langergraber et al. 2010) and the data presented in Tables 15.2 and 15.4, it was calculated that the sizing criterion would be 10.4 and 18 m²/pe for the whole system, and 1.7 and 2.9 m²/pe only for the VF-CW (periods B and D, respectively), which is within the range presented in the literature 1.5–20 m²/pe as reported by Kadlec and Wallace (2009), Kim et al. (2015) and Boog et al. (2014).

15.4 Conclusions and Outlook

The intensification of the CW performance by integrating a VF-CW with partly saturated bed and a FEM-CW can ensure high removal efficiencies for TN and P-PO₄. The application of artificial intermittent aeration in a VF-CW can additionally allow achieving high removal efficiency of carbonaceous compounds (determined as DOC) without compromising the removal of TN and P-PO₄. The underlying removal mechanisms were not studied but the putative processes were predominantly microbial nitrification-denitrification and plant uptake (especially in the

FEM-CW) for the TN removal, and plant uptake for the P-PO₄ removal. The observed low removal rates (expressed as g/m²d) are attributed to long overall retention time in the system, which was not determined experimentally and will be further optimized. The development of vegetation on the floating mat in the FEM-CW appears to be lengthy process requiring expertise-based selection of plant adapted to specific conditions of the floating buoyant structure. In the presented experiment it was observed that yellow flag (*Iris pseudoacorus*) adapted best to growing on a floating structure in the FEM-CW, which was based on its growth rate and amount of biomass. The establishment of vegetation in the VF-CW was less challenging as giant miscanthus was successfully applied to replace common reed, which was desiccated after a few weeks of operation. The future tasks will include further optimization of the system, but also monitoring of the removal and fate of selected organic micropollutants. It is assumed that the broad set of abiotic and biotic factors influencing the removal of pollutants in the VF-FEM-CW might be particularly attractive for the removal of these compounds.

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