Chapter 16
Treatment of Chlorinated Benzenes in Different Pilot Scale Constructed Wetlands

Zhongbing Chen, Jan Vymazal, and Peter Kuschk

Abstract Chlorinated benzenes (CBs) are common pollutants in groundwater due to their broad usage in industry and agriculture. Remediation of CBs from contaminated groundwater is of great importance. Biodegradation has proved to be a suitable approach in eliminating CBs from polluted water, and constructed wetland (CW) is an alternative as cost efficient technology to remove CBs from wastewater. In the present study, a comparison covering five growing seasons (from May 2006 to November 2010) was carried out among four pilot-scale CWs: (1) unplanted horizontal subsurface flow (HSSF) CW; (2) planted HSSF CW; (3) planted HSSF CW with tidal flow; (4) hydroponic root mat (HRM). The unplanted HSSF CW was not efficient for CBs removal, with removal efficiency less than 23 % for the four CBs, and no capability to remove 1,2-DCB. Planted HSSF CW exhibited significantly better treatment performance than the unplanted HSSF CW, and the CBs removal efficiency can be enhanced to some extend (especially after 3 m from the flow path) when running under tidal flow operation. Highest CBs removal efficiency was reached in the HRM system, with mean removal rates for monochlorobenzene, 2-chlorotoluene, 1,4-dichlorobenzene (DCB) and 1,2-DCB were 219, 0.92, 7.48 and 0.86 mg/m^2/d, respectively. In conclusion, the HRM is the best variant CW to treat chlorinated benzenes, and it can be an option for the treatment of pollutants which prefer aerobic degradation.

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16.1 Introduction

Monochlorobenzene (MCB) is mainly used as a chemical intermediate in the manufacture of organic chemicals, manufacture of pesticides and degreasing solvent in automobile parts. Dichlorobenzene (DCB) isomers are mainly used in the production of medicine, dyes, herbicides and insecticides, normally, they are not found naturally. The widely used chlorinated solvents such as MCB and DCBs are highly persistent in aerobic and anaerobic circumstances, due to improper handling and storage, they are commonly detected pollutants in sediment and groundwater. Most of the chlorinated benzenes (CBs) are toxic to human which have the potential to cause liver, kidney and central nervous system damage. Some of them are listed on US EPA priority pollutants for drinking water regulation, e.g., maximum contaminant level for MCB, 1,2-DCB, and 1,4-DCB are 0.1, 0.6, and 0.075 mg/L, respectively (USEPA 2002).

Constructed wetlands (CWs) have been widely used as an alternative to conventional intensive systems for different types of wastewater treatment because of their lower energy requirements, easy operation and maintenance (Vymazal 2011). In the past two decades, CWs were used for the clean-up of sediments and groundwater contaminated by CBs (MacLeod et al. 1999; Keefe et al. 2004; Braeckevelt et al. 2007a, b, 2008, 2011; Lee et al. 2009; Cottin and Merlin 2010; Schmidt et al. 2014; Chen et al. 2015). In CWs, the main pathways for chlorinated benzenes removal are microbial degradation, volatilization, plant uptake, and sorption (Kadlec and Wallace 2009; Pardue et al. 1999). Both aerobic and anaerobic MCB degradation pathway was convinced by the observation of carbon isotope shift in both the planted and unplanted horizontal sub-surface flow (HSSF) CWs (Braeckevelt et al. 2007b). It was shown that plants can enhance the removal of MCB, which higher MCB removal efficiency was achieved in the planted HSSF CW than in the unplanted HSSF CW (Braeckevelt et al. 2008). Moreover, the planted HSSF CWs obtained higher MCB removal efficiency in upper layer (Braeckevelt et al. 2007a). Volatilization of MCB amounted to only 2–4 % of the total removed MCB (Braeckevelt et al. 2011). Thus, to create more aerobic condition in the CWs will be of great importance for the removal of MCB and DCBs. Tidal flow operation strategy was developed to increase oxygen input in CWs since the later 1990s. During the tidal flow operation, the wastewater acts as a passive pump to repel and draw oxygen into the CWs (Tanner et al. 1999; Green et al. 1997; Sun et al. 1999), therefore, it can improve the aerobic condition in CWs. Due to the lack of substrate, and easy cope with water level, floating hydroponic root mat system has been used for the treatment of different pollutants (Van de Moortel et al. 2010; Headley and Tanner 2012; Chen et al. 2015), including pollutants prefer aerobic degradation.

In the present study, two pilot scale HSSF CWs (one planted and one unplanted) was established to treat groundwater contaminated with CBs at the beginning. In order to enhance the removal performance of CBs, the unplanted system was changed into a hydroponic root mat, and the planted system was running under tidal flow regime to improve the aerobic condition in the HSSF CW. Therefore, the aim of this study was to compare the treatment performance of the four different CWs regarding the elimination of CBs.

16.2 Materials and Methods

16.2.1 Description of Pilot Scale CWs

The unplanted and planted HSSF CWs were established in March 2003 in Bitterfeld Germany. The dimension of the system is 6 × 1 m, filled with local aquifer material up to 0.5 m. The filling material consisted of gravel (25 %), sand (51 %) and silt/clay (3 %), and the hydraulic conductivity is 2.1×10^{-3} m s^{-1}, porosity of 0.28. One of the CWs was planted with common reed (*Phragmites australis*), the other one was left unplanted as a control. More details of the HSSF CWs are described elsewhere (Braeckevelt et al. 2011; Chen et al. 2012). In March 2010, the unplanted HSSF CW was replaced by a hydroponic root mat (HRM), 3-years old well developed plant root mats from *P. australis*, with a porosity of 0.70. In 2010, the planted HSSF CW was run under 1 week tidal regime, which is a fast outflow flushing of 2 h, causing a rapid decrease in the water level from 0.4 to 0.15 m, a refilling (5.0 L h^{-1}) to water level of 0.4 m took about 34 h, and a further interim period of 132 h. Detail description of the HRM and the tidal flow regime were given previously (Chen et al. 2015). Mean inflow concentrations of CBs were given in Table 16.1.

16.2.2 Sample Collection and Analysis

In total, 43, 52, 6, 14 sampling actions were carried out for the unplanted, planted, planted with tidal flow HSSF CW and HRM, respectively. Pore water samples were taken at different distances (0.5, 1, 2, 3 and 4 m) from the inlet and at different depths (0.3, 0.4 and 0.5 m) in the HSSF CW, same distance but only one depth (20 cm) in the HRM. For the analysis of CBs, 10-mL water samples were collected in 20-mL glass flasks (Supelco, Bellefonte, USA), sodium azide solution was added to the samples to inhibit the microbial activity, and the flasks were sealed with Teflon-lined septa (Pharma-Fix-Septum Buty/PFTE 3.0 MM). The concentrations of the CBs were measured by headspace gas chromatography using a HP 6890 gas chromatograph with flame ionization detector (Agilent Technologies, Palo Alto, USA). For headspace analysis a gas volume of 1 ml was injected at an injection

Table 16.1 Mean concentration and load removal rate after 4 m of the inlet, standard deviation was shown in brackets

	Unplanted (n = 43)			Planted (n = 52)			Tidal flow (n = 6)			HRM (n = 14)		
	In	Out	Removal	In	Out	Removal	In	Out	Removal	In	Out	Removal
	mg/L	mg/L	$mg/m^2/d$	mg/L	mg/L	$mg/m^2/d$	mg/L	mg/L	$mg/m^2/d$	mg/L	mg/L	$mg/m^2/d$
MCB	10.6 (1.8)	9.3 (2.2)	46 (58)	10.6 (1.7)	4.6 (2.4)	199 (49)	7.3 (0.7)	2.5 (2.2)	156 (46)	8.1 (1.2)	1.0 (1.2)	219 (40)
1,4-DCB	0.232 (0.067)	0.181 (0.053)	1.61 (1.31)	0.253 (0.074)	0.085 (0.037)	5.32 (2.07)	0.270 (0.023)	0.061 (0.036)	6.58 (0.94)	0.286 (0.037)	0.045 (0.048)	7.48 (1.21)
1,2-DCB	0.035 (0.010)	0.039 (0.013)	–0.08 (0.20)	0.036 (0.010)	0.023 (0.012)	0.53 (0.25)	0.032 (0.003)	0.014 (0.006)	0.61 (0.14)	0.035 (0.005)	0.007 (0.007)	0.86 (0.18)
2-Chlorotoluene	0.025 (0.009)	0.021 (0.007)	0.14 (0.16)	0.029 (0.011)	0.009 (0.005)	0.63 (0.27)	0.037 (0.003)	0.008 (0.004)	0.91 (0.12)	0.037 (0.004)	0.008 (0.007)	0.91 (0.17)

temperature of 250 °C with split 1:5 (measurements in duplicates). The chromatographic separation was achieved with an HP-1 capillary column (Agilent Technologies, Palo Alto, USA) (30 m length × 0.32 mm inner diameter × 5 μm film thickness) with the following oven temperature program: equilibration at 60 °C (60 min), GC oven program 45 °C (1 min), 20 °C/min to 200 °C (2.5 min), 65 °C/min to 250 °C (1 min), and the detector temperature was 280 °C. Helium was used as carrier gas with a flow rate of 1.7 ml/min. The detection limits were 1.3, 2.4, 1.2 μg/L, for MCB, 1,4-DCB, and 1,2-DCB, respectively.

16.2.3 Data Analysis

Removal efficiency based on load was calculated with the consideration of water loss by evaporation and plant transpiration. The decrease of the organic load along the flow path was calculated assuming the water loss followed a linear change. The flow distance and the depth related loads were calculated based on the assumption that the concentrations at each depth represent the concentration of the cross section through which the water of this presumed depth layer flows. Detail calculation equation was described previously (Chen et al. 2015). One Way ANOVA was run in order to test the significant difference on chlorinated benzenes load removal efficiencies at 4 m between the four systems, significant difference was set at $p < 0.05$.

16.3 Results and Discussion

16.3.1 MCB Removal

Significant difference in MCB load removal efficiency (at 4 m) was found between the unplanted HSSF CW and other three systems, and the HRM with other three systems, but not between the planted HSSF CW and the tidal flow HSSF CW (Fig. 16.1). The highest residual MCB mass along the flow path, which is significantly differ from the other three systems (Fig. 16.1), as well as lowest mean MCB load removal rate (46 mg/m^2/d) was observed in the unplanted HSSF CW (Table 16.1). MCB mean removal efficiency increased from 15 % in the unplanted system to 66 % in the planted HSSF CW, and it increased further to 72 % when the planted HSSF CW operated in tidal flow regime. The highest MCB mean removal efficiency of 90 % was obtained in the HRM, with highest mean load removal rate of 219 mg/m^2/d. Although there is no significant difference on load removal efficiency at 4 m between continuous flow and tidal flow in the planted HSSF CWs, the tidal flow operation can enhance MCB removal efficiency at the last half part of the wetland (after 3 m). No significant difference of MCB load was found among the three depths in the unplanted HSSF CW, but significant difference was found

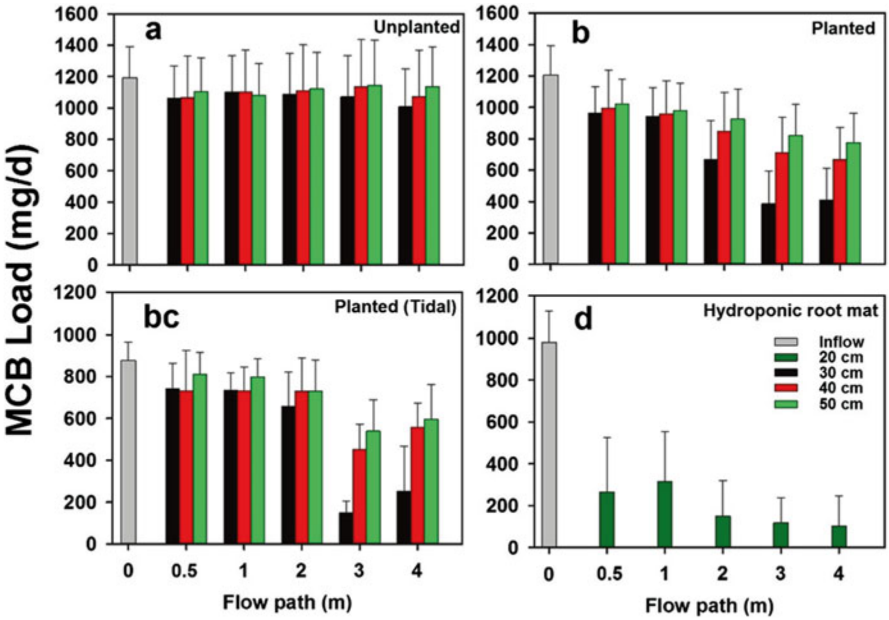

Fig. 16.1 Mean MCB mass load along the flow path in the four systems (n=43, 52, 6, 14 for unplanted, planted, tidal flow and HRM). "*abcd*" was shown as significant difference between the four system

regarding depth in the continuous flow and tidal flow planted HSSF CW, with lower MCB load was observed in the upper layer. This confirms that the vegetation has positive effect on MCB removal, which is due to the release of oxygen by the plant roots, and it thus influence the microbial community. However, anaerobic microbial degradation of MCB may be occur in all the four systems as it was proven that ferric iron and nitrate can stimulate the mineralisation of MCB (Schmidt et al. 2014). But, the MCB dechlorination process can be neglect because no benzene accumulation was detected in all the four systems.

Volatilization is a subordinate removal pathway for MCB removal in the HSSF CW, as it's calculated that maxima MCB emission rate is 13.5 mg/m^2/d, which is less than 4 % of the total removed MCB (Braeckevelt et al. 2011). In a large scale surface flow CW, MCB emission rate of 4 μg/m^2/d was reported, which accounts for 89 % of the total removal (Keefe et al. 2004). However, it should be note that the MCB inflow concentration is only 0.03 μg/L in that study, which is much lower than in previous study (17.6 mg/L). Higher MCB volatilization might be taken place in the HRM, as slightly higher benzene volatilization was observed in HRM (3 %) than in the HSSF CW (1.1 %) (Chen et al. 2012). This is due to the lack of soil coverage in the HRM compare to HSSF CW, where the soil can prevent the direct emission of pollutants from the pore water. Moreover, slightly higher MCB emission may be expected in the tidal flow HSSF CW due to the variation of water levels. Adsorption may take place at the beginning of the addition of CBs, sorption and

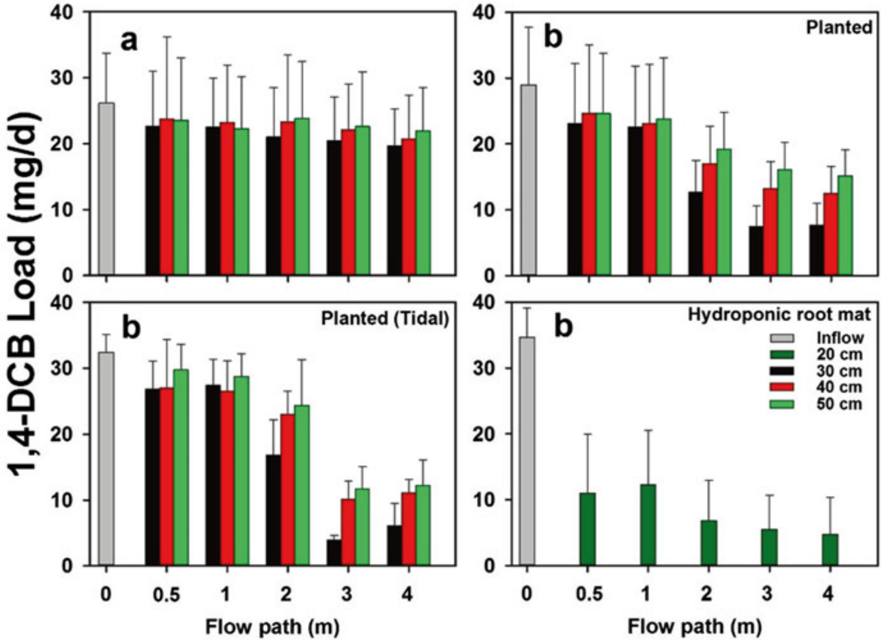

Fig. 16.2 Mean 1,4-DCB mass load along the flow path in the four systems (n = 43, 52, 6, 14 for unplanted, planted, tidal flow and HRM). "*abcd*" was shown as significant difference between the four system

desorption-resistance on biodegradation will coexist afterwards. MCB initial mineralization rates of 0.14 μg/L/h and 1.92 μg/L/h was found in marsh soil and wetland soil respectively, which indicate that microbes associated with MCB degradation can access to the adsorbed MCB, even the desorption resistant part of the sorbed MCB also can be degraded (Lee et al. 2009).

16.3.2 DCBs Removal

There is significant difference in 1,4-DCB load removal efficiency (at 4 m) between the unplanted HSSF CW and other three systems, but no significant difference among the planted HSSF CW, the tidal flow HSSF CW and the HRM (Fig. 16.2). The mean load removal efficiency for 1,4-DCB are 23, 72, 81, and 87 % in the unplanted HSSF CW, the planted HSSF CW, the tidal flow HSSF CW and the HRM, respectively. The residual 1,4-DCB mass decreased significantly along the flow path in the three planted systems, but not in the unplanted system. This testified that the plants can enhance 1,4-DCB removal. Moreover, our results give a higher concentration level for *Phragmites australis* to treat CBs, as other research only gives a concentration of 0.2 mg/ L MCB and 0.2 mg/ L DCB (Faure et al. 2012). The

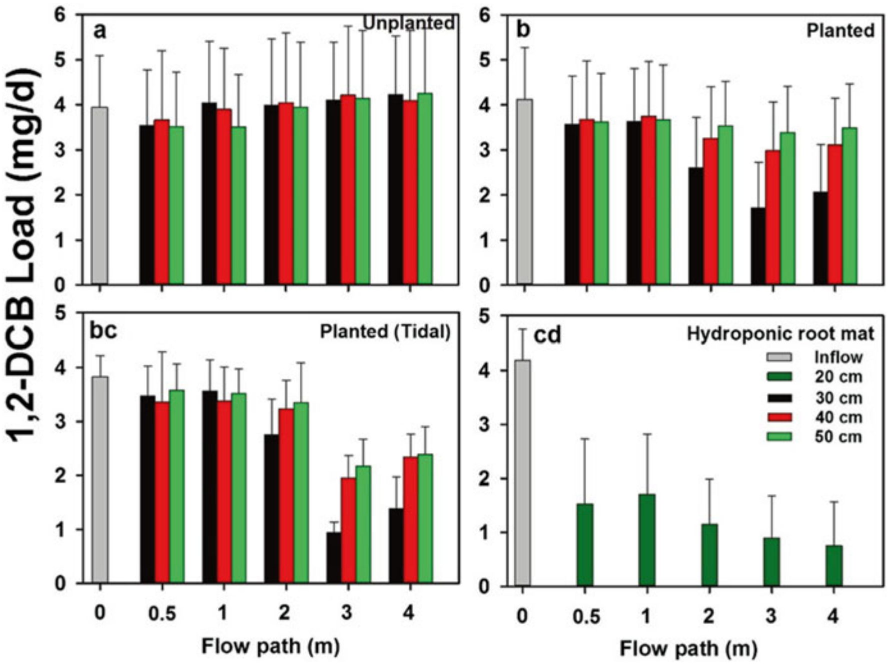

Fig. 16.3 Mean 1,2-DCB mass load along the flow path in the four systems (n = 43, 52, 6, 14 for unplanted, planted, tidal flow and HRM). "*abcd*" was shown as significant difference between the four system

highest mean removal rate for 1,4-DCB is 7.48 mg/m²/d in the HRM, which is much higher than in a surface flow CWs reached 0.11 mg/m²/d with inflow concentration of 0.74 μg/L (Keefe et al. 2004). Moreover, the volatilization of 1,4-DCB is extremely high which can contribute to 95 % of the total 1,4-DCB removal in the surface flow CW (Keefe et al. 2004). This is due to the direct volatilization from water surface, while such extensive volatilization is not expected to take place in our systems because they are subsurface flow with the coverage of soil and density plant root mat.

Load removal efficiency of 1,2-DCB is significantly different between the unplanted HSSF CW and other three systems, between the HRM with the unplanted and planted HSSF CW, but no significant difference between the tidal flow HSSF CW and the HRM, and no significant difference between the planted HSSF CW and the tidal flow HSSF CW (Fig. 16.3). The results showed that 1,2-DCB is difficult to be removed than 1,4-DCB in CWs. It seems that 1,2-DCB almost can't be removed in the unplanted HSSF CW, and mean removal efficiency are 50, 64 and 83 % for the planted HSSF CW, the tidal flow HSSF CW and the HRM, respectively. In principal, DCBs can be dechlorinated to MCB under anaerobic condition. However, this process is negligible in our study due to the relatively lower DCBs concentrations than MCB concentration in the influent.

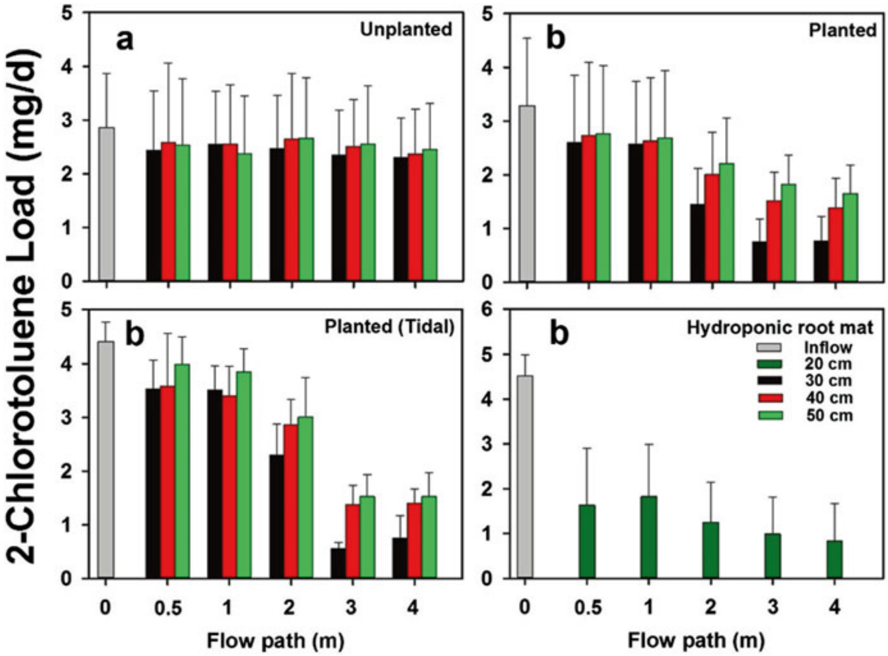

Fig. 16.4 Mean 2-Chlorotoluene mass load along the flow path in the four systems (n = 43, 52, 6, 14 for unplanted, planted, tidal flow and HRM). "*abcd*" was shown as significant difference between the four system

DCBs may be less volatile than MCB due to the lower Henry's coefficients (20 °C) for 1,2-DCB, 1,4-DCB, and MCB are 0.0012, 0.0015 and, 0.00356 atm m^3/mol, respectively (USEPA 2002). Therefore, volatilization for 1,2-DCB and 1,4-DCB in the all the four systems may only account for small portion of the total removal. It was reported that less than 0.15 % of DCB was removed through volatilization in lab scale CWs (Cottin and Merlin 2010). Plant uptake is a potential pathway for CBs removal. A bioconcentration factor of 14 was reached for plant uptake of 1,4-DCB after 7 days, and uptake/translocation of CBs are depend on the CBs hydrophobicity, solubility and volatility (San Miguel et al. 2013). Therefore, a higher plant uptake of CBs in the HRM than in the planted HSSF CWs can be expected, especially in the roots which have direct contact with the wastewater.

16.3.3 2-Chlorotoluene Removal

The behaviour of 2-chlorotoluene in the four systems are similar as 1,4-DCB, which the load removal efficiency (at 4 m) is significant different between the unplanted HSSF CW and other three planted systems, but no significant difference between the three planted systems (Fig. 16.4). The mean removal efficiencies of

2-chlorotoluene in the four systems are comparable to MCB's removal efficiencies, with 16, 76, 83, and 82 % in the unplanted HSSF CW, the planted HSSF CW, the tidal flow HSSF CW and the HRM, respectively. In general, the biodegradation of the chlorinated benzenes is slower under anaerobic than under aerobic conditions. Therefore, the three plant systems exhibited significantly higher removal efficiency than the unplanted system, and lower concentration was detected in the upper layer than in the deeper layer due to the oxygen release by plants.

16.4 Conclusions

It can be concluded that plants can enhance the removal of chlorinated benzenes in HSSF CW, and tidal flow operation is a useful approach to enhance the treatment efficiency of CBs. The HRM system obtained the highest removal efficiencies for most of the CBs, and due to the lack of substrate, it can be a cost-efficient alternative technology for wastewater treatment, especially for pollutants prefer aerobic degradation.

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