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RECENT ADVANCES AND NOVEL CONCEPTS IN ENVIRONMENTAL TECHNOLOGIES

Optimization of reactive media for removing organic micro-pollutants in constructed wetland treating municipal landfill leachate

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Abstract
The removal of organic micro-pollutants (OMPs) from landfill leachate in constructed wetland (CW) media having different material mixtures of sand (S), clay (C), and iron powder (Fe) was investigated using experimental column study. The use of S:C:Fe media consisting of 60:30:10% (w/w) and cattail as vegetation was found optimum for the removals of 2,6-DTBP, BHT, DEP, DBP, and DEHP at 67.5–75.4% during long-term operation of 373 days. Adsorption and biodegradation were confirmed as predominant mechanisms for their removal in CW media but their contribution in total removal varied depending on chemical properties of OMPs. Adsorption kinetic could be well explained by pseudo-second-order whereas biodegradation kinetic followed first-order reaction. The adsorption affinity of OMPs to CW media was S:C:Fe > S:C > S in descending order. This study demonstrated high and sustainable removal of OMPs during long-term operation of CW with the optimized reactive media.

Keywords Clay · Constructed wetland · Iron powder · Landfill leachate · Phenolic compounds · Phthalic acid esters · Reactive media

Introduction

Disposal of municipal solid wastes in landfills is commonly practiced in many developing countries. The operation of municipal solid waste landfills can create adverse environmental impact such as leachate which may contain many toxic compounds including organic micro-pollutants (OMPs) such as phenolic compounds and phthalic acid esters (PAEs). These OMPs are commonly used as plasticizers in plastic products and other materials such as liquor, insect repellent, and cosmetics (Qi et al. 2018). The phenolic compounds which are commonly used in commercial products are bisphenol A, 2,6-di-*tert*-butylphenol, 2,6-di-*tert*-butyl-4methylphenol, and 2-chlorophenol and they are classified as carcinogenic substances. Phthalic acid esters (PAEs), i.e., ethyl phthalate, butyl phthalate, and bis (2-ethylhexyl) phthalate, are classified as toxic compounds on the endocrine system of human bodies and have adverse reproductive system outcomes, neurodevelopmental, and effects on the immune system in both humans and wildlife. These compounds have been reported in many countries and detected at a higher concentration in leachate from municipal solid waste landfills (Slack et al. 2005) as well as increasingly emerged in the environment (Luo et al. 2014).

In order to minimize pollution from leachate, proper treatment prior to its discharge from the landfill area is required. Constructed wetlands (CWs) have been applied as a low cost technology for the treatment of landfill leachate with good purification effects in terms of organic and nutrients (Bulc 2006). Major organic removal mechanisms in CWs are sedimentation and filtration of suspended solids in the gravel bed, plant uptake, and biological decomposition processes. The mechanisms responsible for nutrient removal are ammonia volatilization, plant uptake, and microbial transformation (Saeed and Sun 2012). CWs have also been investigated on their capacities to remove OMPs. Dan et al. (2017) reported wide variations in the removal efficiencies of phenolic

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compounds, i.e., phenol (88–100%), 4-*tert*-butylphenol (4-*t*-BP) (18–100%), and bisphenol A (BPA) (9–99%) from synthetic landfill leachate in lab-scale CWs. Moderate removals of BPA (73.3%) and nonylphenols (62.8%) were also achieved in CWs treating domestic wastewater (Toro-Vélez et al. 2016). Meanwhile, multi-stage CWs could provide more than 99% removal of dibutyl phthalate (Zhao et al. 2004). The production of specific enzyme for the biodegradation of OMPs presented in wastewater at low concentrations in CWs was reported (Qi et al. 2018). However, few reports of the relevant literatures have described the removal of OMPs from leachate in CWs especially during long-term operation (Dan et al. 2017).

Several factors such as flow regime, media type, and hydraulic loading rates were found influencing the removal of OMPs in CWs (Tang et al. 2015). Among them, the media play a vital role in regulating the removal of OMPs. In conventional CW, the main pollutant removal mechanisms are adsorption, precipitation, and filtration whereas biological assimilation and plant uptake can also play a significant role (Ge et al. 2015). Among them, adsorption processes are not significantly observed as inert gravel media has low adsorption capacity especially for nutrients and trace pollutants (Keffala and Ghrabi 2005; Tang et al. 2015). In order to enhance its adsorptive removal capacities, proper substrates with specialized physicochemical properties to targeted pollutants should be incorporated (Calheiros et al. 2008). Recent advancement in CW development aims at replacing conventional media with materials with higher adsorption capacity, e.g., zeolites for ammonium removal (Mojiri and Ahmad 2017; Hou et al. 2018) and zeolites-slag for adsorption and precipitation of heavy metals (He et al. 2017). Clay material is one of the natural adsorbents that has been used in CW (Dordio and Carvalho 2013). It possesses negative charge which is balanced by exchangeable cations. Clay support matrix can enhance OMP removals such as pharmaceuticals, phenoxy acids, and phthalate (Dordio et al. 2007; Dordio and Carvalho 2013; Wu et al. 2015). Meanwhile, iron powder could promote oxidative reaction, adsorption, and precipitation (Kang and Choi 2008; Boparai et al. 2011; Shimizu et al. 2012). The use of Fe^0 or ZVI also concerns the directional transfer of electrons from Fe to the pollutants that transform the latter into less toxic or non-toxic species (Fu et al. 2014; Ezzatahmadi et al. 2017). It is therefore also efficient for OMP removals (Takayanagi et al. 2017; Perini et al. 2014; Huang et al. 2017).

CW utilizing reactive media have been developed for remediation of landfill leachate (Chiemchaisri et al. 2015). This reactive media containing sand, clay, and Fe-based waste materials were employed to enhance the performance of CWs. Clay soil has been used as a barrier to limit migration of hazardous pollutants from the landfill area (Cuevas et al. 2012; Zhan et al. 2014; Zhou et al. 2014). Fe waste materials in the forms of sludge or slag, as well as zero-valent iron (ZVI), have been examined for the treatment of landfill leachate targeting major or macro-pollutants (Chiemchaisri et al. 2015; Wijesekara et al. 2014; He et al. 2017) or utilized as permeable reactive barrier (Dong et al. 2009, Van Nooten et al. 2008; Zhou et al. 2014). However, the understanding of their effect on the removal of OMPs is not well established.

In this study, CW reactive media targeting for the removal of OMPs present in landfill leachate, i.e., phenolic compounds and PAEs, was investigated in lab-scale column experiment. Their removal mechanisms in the CW media were clarified in batch experiments. This investigation will be helpful to provide proper design of CW media to enhance the removal of OMPs as well as provide as potential management options that could be used to alleviate pollution arising from municipal solid waste landfills.

Materials and methods

Experimental setup and operation

The experimental columns (Fig. S1) made of PVC having 0.15 m diameter and 0.50 m height were used. They were filled with media having different compositions of sand (S), clay (C), and iron powder (Fe) as presented in Table 1. The investigation was carried out in 3 separate experiments. In the 1st experiment (Exp. I, 119 days), the weight percentages of sand and clay in media were varied at 100:0 (A), 70:30 (B), 60:40 (C), and 50:50 (D). Subsequent experiment (Exp. II, 112 days) was conducted using appropriate S:C ratios obtained from Exp. I while introducing Fe to replace C in the media at different levels, i.e., having S:C:Fe of 70:20:10 (E), 60:35:5 (F), 60:30:10 (G), and 60:20:20 (H). Then, long-term experiment (373 days) was performed to investigate the performance of the best reactive media obtained from Exp. II compared with the best non-Fe media (obtained from Exp.I) and sand media (A). They are called sand (S), sand-clay mixture (S:C), and sand-clay-iron powder (S:C:Fe) media respectively. This long-term experiment was initially performed under no plant condition during day 0–172 then followed by introduction of *Typha sp.* (Cattail) of one shoot each to the experimental columns during day 173–373. Synthetic light was supplied through light bulbs installed at the top of columns (1.0 m above media surface) for plant growth, providing a constant light intensity of about 35,000 lx.

In order to verify the contribution of each material in CW media mixture to the treatment of pollutants, short-term column experiments using individual media component were performed. The setup of column for examining these individual materials was identical to those of column experiments mentioned above. The results obtained from this preliminary investigation are provided in the supplement (Table S2).

Table 1 Characteristics and operating conditions of media used in column experiments

Exp	Media	S:C:Fe[a]	Porosity (%)	BET surface area (m^2/g)	CEC (cmol/kg)	Feed flow rate (l/d)[b]	Permeability (cm/s)
I	A	100:00:00*	37.00	1.16	1.21	0.327	$7.42*10^{-4}$
	B	70:30:00	39.70			0.354	$6.97*10^{-4}$
	C	60:40:00*	43.00	13.06	7.60	0.380	$3.12*10^{-4}$
	D	50:50:00	48.60			0.424	$1.97*10^{-5}$
II	E	70:20:10	40.55			0.362	$1.14*10^{-4}$
	F	60:35:5	42.60			0.380	$1.62*10^{-5}$
	G	60:30:10*	41.00	18.29	18.2	0.362	$2.93*10^{-4}$
	H	60:20:20	47.40			0.415	$1.64*10^{-5}$

[a] S:C:Fe refers to weight percentages of sand, clay, and iron power in media

[b] Feed flow rate set to achieve empty bed HRT of 6 days

* Media used in long-term experiment

The columns were fed with real leachate obtained from a landfill site in Thailand. Leachate was taken directly from the storage pond at which leachate was collected from operating and closed area of the site. It was transported and stored under cool condition (4°C) prior to its use in laboratory experiment. The feed rate to each column was adjusted according to the characteristics (porosity) of CW media so that empty bed hydraulic retention time (HRT) in all columns was set equally at 5 day.

Sample analyses and performance evaluation

The chemical characteristics of influent and effluent were analyzed in terms of pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), ammonia nitrogen (NH_3), and total kjeldahl nitrogen (TKN). All the analyses were performed according to Standard Methods for the Examination of Water and Wastewater (APHA 2012). TOC were analyzed using a TOC-VCSH analyzer (Shimadzu, Japan). The treatment performance in each experimental column was evaluated based on mass removal efficiency (RE) of organic (BOD, COD, TOC), nitrogen (NH_3, TKN), and OMPs as described in Eq. (1).

$$\mathrm{RE}(\%) = \frac{(C_0Q_0)-(C_iQ_i)}{(C_0Q_0)}x100 \quad (1)$$

where C_0, C_i is influent and effluent concentration and Q_0, Q_i is volume of influent and effluent, respectively.

Media properties were also evaluated in terms of its hydraulic permeability using constant head method, carbon (C), and nitrogen (N) contents using CHNS/O 2400 Analyzer (Perkin Elmer), dissolved oxygen (DO), and absorbed OMPs. The plant growth was measured in terms of plant height, stem density, and dry weight of the above-ground biomass (leaves and stems) and absorbed OMPs. Relative growth rate (RGR) of plant was evaluated by the following equation (Eq. 2)

$$RGR = \frac{InW_e - \ln W_b}{t_e - t_b} \quad (2)$$

where W_b (g) and W_e (g) are dry biomass at the beginning of the experiment (t_b) and the end of the operation (t_e), respectively.

The major OMPs found in leachate samples in this study are 2,6 DTBP, BHT, DEP, DBP, and DEHP. Their physio-chemical properties are shown as Table S1. Their concentrations were determined using solid phase extraction technique (SPE) followed by gas chromatography-mass spectrometry (GC/MS) analyses. To determine their concentrations in soluble form, the waters obtained after separation of suspended solids by GF/C filtration were used. The VertipakTM-C18 tubes were used for micro-pollutant extraction. First, SPE tubes were cleaned with 10 ml dichloromethane: methanol mixture (1:9 *v*/v ratio) and followed by 10 ml pure water and 100 ml water samples respectively. The SPE tubes were left for drying with clean air and the eluted with 15 ml of dichloromethane: methanol mixture. The fraction of the elution step was concentrated by evaporation with pure nitrogen gas. Each final extract was then kept in a 2-ml glass vial at − 20 °C until analysis by GC-MS (Shimadzu, GC-MS-QP2010 plus).

For determination of OMPs in media and plant samples, 10 g of sample was put into a glass bottle and mixed with 20 ml dichloromethane: methanol mixture and left overnight followed by sonication for 15 min then filtered through a Whatman GF/C filter paper (0.7 μm). The solvent was then transferred to C18-SPE tubes and eluted with 5 ml of dichloromethane: methanol mixture. Then, the fraction elution step was concentrated and stored (− 20 °C) until analyzed by GC-MS.

Mass balance analysis of OMPs

Mass balance analysis was used to assess mass removal capacity of the CWs under different conditions (Chen et al. 2016).

$$M_i = C_i Q(or M)\, T \quad (3)$$

Where M_i is the mass loading of the pollutant in the water, substrate, and plant; C_i represents the concentration of the pollutant in the water, media, and plant; Q is the daily water flow into the CWs; M is the dry weight of the media or plants; and T is the operation time of the CWs

$$M_{\mathrm{removal}} = M_{\mathrm{influent}} - M_{\mathrm{effluent}} \quad (4)$$

Where $M_{influent}$ and $M_{effluent}$ are the mass loadings of pollutant in the influent and each CWs effluent, respectively and $M_{removal}$ the mass removal of the pollutant after CWs treatment.

$$M_{\mathrm{removal}} = M_{\mathrm{media}} + M_{\mathrm{plant}} + M_{\mathrm{loss}(\mathit{biodegradation})} \quad (5)$$

Where M_{media} and M_{plant} are the mass loading of a pollutant adsorbed by media and plants, respectively and M_{loss} is the mass loadings of a pollutant degraded by microorganisms.

Kinetics of OMP removal

The batch experiments were performed in 2 separate sets. Initial experiments were carried out to examine COD, TKN, and OMP removal capacities of S, C, and Fe media. Subsequent experiments were carried out to quantify adsorption and biodegradation capacities of CW media, i.e., S, SC, and SCFe media at the beginning (day 0) and the end (day 373) of long-term column experiment for targeted OMPs. All batch experiments were performed using 1 g media in 100 ml volume of leachate having initial concentrations of 865 mg/l of COD, 32 mg/l of TKN, 326 μg/l of 2,6-DTBP, 420 μg/l of BHT, 145 μg/l of DEP, 620 μg/l of DBP, and 2250 μg/l of DEHP. In the experiments using CW media from long-term experiment, two conditions of media were prepared, i.e., active and inactive media to distinguish the removal via adsorption by inactive media from total removal (adsorption + biodegradation) by active media. For inactivation of microbial activities, the media were repeatedly autoclaved at 121 °C. The batch experiments were performed at room temperature under shaking condition (200 rpm) and the samples were taken for analysis at different times, i.e., 0, 1, 2, 3, 4, 6, 12, and 24 h. They were centrifuged at the speed of 7,000 rpm for 10 min then the supernatant was used for OMP analyses. The absorbed amounts of OMPs were calculated from the difference between the initial concentration and the final equilibrium concentration in the aqueous phase.

Statistical analysis

The statistical analysis was carried out using Microsoft Excel to obtain averages and standard deviations of concentrations of pollutants and their removal efficiencies. One-way ANOVA was used to evaluate the statistical significance of the difference between the experimental conditions using SPSS version 22.0 (IBM).

Results and discussion

Optimization of CW media

The results from column experiments using individual CW media components revealed the superiority of iron powder compared to clay and sand materials (Table S2). There was a significant improvement ($p < 0.05$) in the organic (BOD, COD, TOC), nitrogen (NH_3, TKN), and OMP removals when iron powder was used as the media compared to sand. Meanwhile, significant improvement of organics and OMPs from clay was also observed. In batch experiments, adsorption capacities of COD were 48.1 mg/g for iron powder, 38.7 mg/g for clay, and 32.4 mg/g for sand. Much lower adsorption capacities of TKN at 1.5, 1.0, and 0.6 mg/g for iron powder, clay, and sand were observed. For OMPs, the highest removal was observed for DEHP in iron powder media (134.6 μg/g) followed by its removals in clay (92.0 μg/g) and sand (35.5 μg/g) respectively. Meanwhile, the removals of DEP were found lowest (2.2–3.8 μg/g) in the CW media. For all OMPs studied, their removals in iron powder were about 1.2–3.8-fold of those in clay and sand media. Thus, the incorporation of reactive (iron powder, clay) material into CW media could potentially improve the treatment performance from conventional (inert media) CW.

Table 2 shows the removals of organics, nitrogen, and OMPs from landfill leachate with CW media having different material compositions. The effect of clay composition in CW media was observed by comparing the pollutant removal efficiencies between A and D columns. In sand media (A) column, average organic matter removal in terms of BOD, COD, and TOC was 62.9%, 49.4%, and 60.5%, respectively. When clay material was introduced at 30% (B), 40% (C), and 50% (D) in CW media, their removals increased to 65.1–71.8% for BOD, 55.4–64.5% for COD, and 63.7–69.9% for TOC. Statistical difference in organic removal was found between A and C columns suggesting that introduction of clay material at 40% or more helped improving organic removal at a significant level ($p < 0.05$). The incorporation of clay mixture into CW media helped improving the removal organic pollutants through adsorption and biodegradation mechanisms, both of which were supported by a significant increase in specific surface area of CW media when clay material was included (Table 1). In landfill leachate, the organic compounds with large and complex molecular structure could be easily adsorbed onto CW media. Sato et al. (2005) reported that the removals of organic matter in soil matrix took place

Table 2 Organic, nitrogen, and OMPs removal efficiencies in CW media with different compositions

Parameter	Inf.	Mass removal (%)—Exp. I				Inf.	Mass removal (%)—Exp. II			
		A	B	C	D		E	F	G	H
BOD (mg/l)	157 ± 28	62.9 ± 6.3^{c}	65.1 ± 7.2	67.8 ± 8.0	71.8 ± 8.8^{c}	149 ± 19	69.1 ± 7.1^{f}	73.2 ± 6.3	76.3 ± 5.0^{f}	70.8 ± 11.5
COD (mg/l)	716 ± 207	$49.4 \pm 6.9^{b,c}$	55.4 ± 8.0^{d}	$64.5 \pm 7.0^{b,d}$	60.9 ± 11.0^{c}	591 ± 90	$59.8 \pm 6.8^{e,f,g}$	$66.0 \pm 6.3^{e,h}$	$70.2 \pm 6.1^{f,h}$	64.4 ± 10.7^{g}
TOC (mg/l)	212 ± 42	$60.5 \pm 6.1^{b,c}$	63.7 ± 5.3^{d}	$69.9 \pm 3.7^{b,d}$	67.3 ± 6.8^{c}	205 ± 38	$61.7 \pm 6.2^{e,f}$	$69.8 \pm 4.2^{e,h}$	$74.7 \pm 4.5^{f,h}$	69.4 ± 9.3
NH_3 (mg/l)	8 ± 1	$44.4 \pm 10.5^{b,d}$	49.2 ± 10.3	$59.9 \pm 9.3^{b,d}$	52.3 ± 11.3	10 ± 2	57.7 ± 8.0^{f}	62.2 ± 8.2^{h}	$72.6 \pm 7.6^{f,h}$	62.7 ± 17.2
TKN (mg/l)	43 ± 10	$43.4 \pm 6.4^{a,b,c}$	$50.0 \pm 7.6^{a,d}$	$60.2 \pm 7.9^{b,d}$	55.8 ± 9.9^{c}	42 ± 5	54.9 ± 13.0^{f}	66.1 ± 11.4	69.0 ± 10.8^{f}	55.9 ± 14.3
DEP (μg/l)	144 ± 18	$48.2 \pm 6.5^{b,c}$	54.9 ± 5.8^{d}	$61.5 \pm 6.9^{b,d}$	58.4 ± 10.0^{c}	150 ± 13	$55.8 \pm 5.6^{e,f,g}$	$63.1 \pm 4.9^{e,h}$	$67.5 \pm 6.0^{f,h}$	65.0 ± 12.6^{g}
DBP (μg/l)	480 ± 60	$48.3 \pm 5.3^{b,c}$	52.0 ± 6.0^{d}	$59.4 \pm 6.8^{b,d}$	57.6 ± 11.2^{c}	510 ± 25	$52.5 \pm 5.1^{e,f,g}$	$61.0 \pm 5.8^{e,h}$	$65.0 \pm 5.5^{f,h}$	62.9 ± 12.7^{g}
2,6-DTBP (μg/l)	347 ± 65	$42.4 \pm 4.8^{a,b}$	47.4 ± 7.2^{a}	56.3 ± 7.4^{b}	55.0 ± 11.0	352 ± 39	$51.7 \pm 7.3^{e,f,g}$	60.4 ± 5.9^{e}	62.2 ± 7.0^{f}	60.8 ± 12.0^{g}
BHT (μg/l)	411 ± 72	$48.5 \pm 6.2^{a,b,c}$	$53.4 \pm 6.9^{a,d}$	$60.3 \pm 7.4^{b,d}$	58.3 ± 8.4^{c}	431 ± 84	$54.6 \pm 4.8^{f,g}$	58.5 ± 4.9^{h}	$66.0 \pm 4.5^{f,h}$	60.7 ± 12.9^{g}
DEHP (μg/l)	1074 ± 168	$41.4 \pm 5.5^{a,b,c}$	$48.5 \pm 6.4^{a,d}$	$56.0 \pm 8.6^{b,d}$	57.5 ± 9.7^{c}	1410 ± 279	$52.0 \pm 5.0^{f,g}$	56.2 ± 5.0^{h}	$63.9 \pm 5.2^{f,h}$	61.1 ± 12.3^{g}

The values shown are average ± SD of influent (Inf) concentrations and mass removal (%)

a, b, c, d, e, f, g, or h denotes significant difference ($p < 0.05$) in the removal efficiency between each pair of experiments through filtration and adsorption mechanisms during initial period after which biodegradation of organic matter gradually enhanced through the development of microbial activities.

In terms of nitrogen (NH_3 and TKN), their removals were increased from 43.4% and 44.4% (for A) to 59.9% and 60.2% (for C). Statistical significant increase in their removals was also observed when 40% of clay materials were incorporated into CW media. TKN removal could be initially promoted through adsorption onto the media even through at much smaller extent than COD. Its adsorptive removal in sand is quite limited since inert media has low adsorption capacity (Keffala and Ghrabi 2005). Meanwhile, elimination of NH_3 was mainly occurred through microbial conversion. When the soil was incorporated into the media, adsorptive removal of TKN was slightly increased due to an increase in surface area of media. However, it was reported that the removal of TKN could be enhanced in soil through the presence of microbial activities as when it was hydrolyzed to ammonia and subsequently converted to nitrate by the soil could be restored for successive adsorption (Zhang et al. 2005). Previous research has also demonstrated that long-term operation using silty clay media has promoted the growth of nitrogen transforming microorganisms, i.e., *Bacillus*, *Pseudomonas*, *Acinetobacter*, *Hyphomicrobium*, and *Nitrosomonas* sp. yielding improvement of nitrogen removal (Sun et al. 2018).

For OMPs, their removals in sand media were found between 41.5 and 48.5%. Higher mass removals were observed for 2,6-DTBP, BHT, and DEHP than those for DEP and DBP. These results suggested the adsorption of hydrophobic compounds in sand media played important role in their removals. Similar observation was reported in Tang et al. (2015). Meanwhile, their removals were found to significantly increase when clay materials were introduced into media at 40%. The highest removals of DEP, DBP, 2,6-DTBP, BHT, and DEHP were observed at 61.5%, 59.4%, 56.3%, 60.3%, and 56.0% respectively. The introduction of clay material improved the removal of OMPs through adsorption as the specific surface area of CW media was increased (Liu et al. 2013; Minling et al. 2015; Wu et al. 2015). In soil, OMPs could be removed through initial surface adsorption followed by gradually entering into soil organic matter and small pore of soil particles where the biodegradation took place (Minling et al. 2015). Clayey soil has high potential to absorb OMPs due to its high OM and CEC properties, thus providing positive influence on OMP adsorption as there are special sites in humic acid that can bound with OMPs (Minling et al. 2015). The removal of DBP in CW media soil has been strongly correlated with the presence of microbial activities (Zhou et al. 2005; Liang et al. 2009).

From the above results, it was found that C and D media provided better treatment performance than the others and considered to be appropriate ones for the operation. Among them, hydraulic characteristics of the media also have vital role for the sustainability of long-term CW operation. During the experiment, it was found that the water infiltration rates of C media decreased by 28.7% as its permeability was reduced to $1.90*10^{-5}$ cm/s after 119 days. Meanwhile, the D media had its water infiltration rate reduced by 44% with permeability reached $1.34*10^{-6}$ cm/s just after 84 days of operation as clogging of media took place. Therefore, C media with 60% sand and 40% clay was found to be the most appropriate media in experiment I.

Subsequent experiments (Exp. II) were carried out to investigate the effect of iron powder replacing clay material in CW media (E to H columns). As shown in Table 2, the E column provided the worst performance as their coarse (sand) and fine (clay and iron powder) material percentages were not set at the optimum condition obtained from Exp. I (60:40%). In the other 3 columns, the percentage of iron powder was increased from 5% (F) to 10% (G) and 20% (H) while the sand percentage was fixed at 60%. Among them, the G column provided the highest mass removals of organic, nitrogen, and OMPs at significant level ($p < 0.05$) from other media. At this optimum material ratio, the highest average mass removals of organics (76.3% for BOD), nitrogen (72.6% for NH_3), and OMPs (62.2–67.5%) were achieved during 112 days of operation.

From the above results, it was clearly shown that the incorporation of iron powder helped improve the removals of organics, nitrogen, and OMPs in CW media. The inclusion of iron power at 10%, replacing clay materials, yielded best results. Iron powder can help remove organics from water through formation of iron-organic complex (Chiemchaisri et al. 2015) through co-precipitation via oxidation-reduction reaction (Zhou et al. 2014). The presence of iron oxide/hydroxide layer through oxidation of iron powder could provide favorable adsorption site for cation through electrostatic attraction (Takayanagi et al. 2017). This phenomena would also enhance adsorptive removal of NH_4^+. Moreover, there were also recent reports on beneficial effect of the presence of iron oxide and ZVI on promoting biological nitrogen removal (Li et al. 2018, Guo et al. 2019). During the experiment, it was also noticed that the operation of H column (20% Fe) faced some difficulties in facilitating water penetration it as its permeability dropped down to $5.15*10^{-7}$ cm/s just after 64 days. The clogging of media took place as excessive amount of iron powder adsorbed water, then oxidized into iron precipitate and agglomerated with clay resulting in a cementitious material. Therefore, the amount of iron powder included in CW media should be limited and its optimum amount of 10% was recommended from this study. Comparing the OMP removal among the experimental columns, the results reveal that iron powder promoted their removals regardless of their hydrophobicity. For hydrophobic compounds, iron powder helped improve physical structure of media providing more adsorption site (Table 1) while forming iron-organic complex (Chiemchaisri et al., 2015) which enhanced their removals.

The clay zero-valent iron composite materials possess high removal capacities and fast degradation rates of pollutants (Ezzatahmadi et al. 2017). Moreover, iron powder or ZVI also reported to support organic and nitrogen (Dong et al. 2009; Zhang et al. 2019) and OMP removals (Perini et al. 2014) through enhanced microbial activities.

Long-term performance of CW media

Figure 1 shows long-term organic and nitrogen removals in CW having sand (S), sand: clay (S:C) and sand: clay: iron powder (S:C:Fe) media. During day 0–172, the system was initially started up without plant. Subsequent operation was performed with cattail as vegetation during day 173–373. In sand media (S) column, average mass removals of BOD and COD were 63.7% and 49.3%. Meanwhile, NH_3 and TKN removals were 48.5% and 46.8%. During the start-up period, the organic and nitrogen removals were found relatively lower especially during the development and immaturity of the microbial film on the media surface but they were gradually improving with time. Significant improvement in the removal efficiencies was observed when cattail was introduced. The operation of the S column with vegetation during day 173–373 yields average removals of 72.1% BOD, 61.2% COD, 61.5% NH_3, and 60.3% TKN. In column with sand and clay (S:C) mixture, higher organic and nitrogen removals were observed during the start-up period. Average BOD, COD, NH_3, and TKN removals were 64.1%, 54.7%, 52.1%, and 49.0% respectively. Their removals were improved to 79.7%, 69.4%, 74.6%, and 69.9% during the vegetated period. These results confirmed the beneficial effect of clay material by providing larger surface area for organic adsorption and microbial attachment mentioned in the previous experiments. The use of sand, clay, and iron power (S:C:Fe) in media further increased the removal efficiencies to 78.0% BOD, 69.8% COD, 68.7% NH_3, and 69.2% TKN during non-vegetation period (day 0–172) and 82.3% BOD, 73.6% COD, 79.5% NH3, and 74.0% TKN during vegetation period (day 173–373) respectively.

The introduction of iron powder in CW media helped improving the removals of organic and nitrogen pollutants by 14–22%. Significant improvement of organic and nitrogen compounds in leachate was clearly observed using this reactive media especially during the start-up period. Previous researches have reported that the introduction of steel slag improved COD removal by 6–10% from those of limestone and bamboo charcoal media (Lu et al. 2016) and incorporation of iron material could enhance the treatment efficiencies of CW applied to landfill leachate (He et al. 2017). The organic removal in iron incorporated media could be enhanced by their deposition through adsorption and precipitation in CWs (Zhang et al. 2019) as well as microbial activities of iron oxidizing microorganisms adhering to the iron media (Song et al. 2016; Liu et al. 2018). Moreover, improvement of

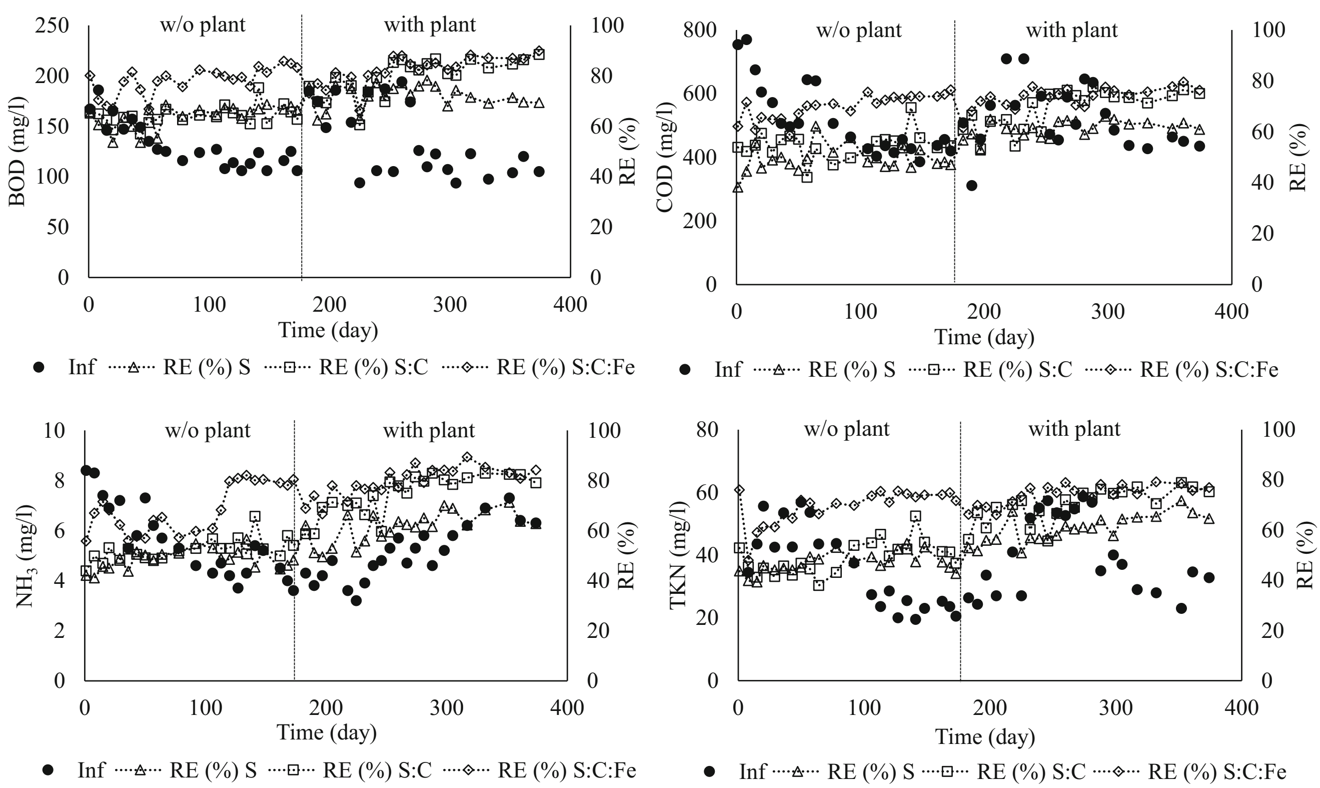

Fig. 1 Organic and nitrogen removals in CW columns during long-term operation

nitrogen removal could be expected through enhanced biological denitrification using iron as electron donor (Dong et al. 2009; Zhang et al. 2019).

Figure 2 shows OMP removal in S, S:C, and S:C:Fe CW columns. During the start-up period, there were 51.8% DEP, 47.2% DBP, 45.1% 2,6-DTBP, 48.6% BHT, and 39.6% DEHP removals in S media on average. Higher removals of 54.3% DEP, 55.0% DBP, 49.9% 2,6-DTBP, 52.4% BHT, and 45.9% DEHP in S:C media and 69.6% DEP, 67.2% DBP, 63.4% 2,6-DTBP, 67.7% BHT, and 59.7% DEHP in S:C:Fe media were achieved. Significant enhancement of OMPs was observed when iron power was incorporated into the media during this start-up period. During long-term operation with cattail as vegetation, their removals in S:C:Fe media were subsequently increased to 80.4% DEP, 77.2% DBP, 70.3% 2,6-DTBP, 73.8% BHT, and 67.5% DEHP respectively. Improvement of OMP removal of 12–20% in the reactive (S:C:Fe) media as compared to the inert (S) media was observed in this study. The introduction of iron powder in media supported their removals initially through adsorption and formation of iron-organic complex while allowing microbial growth and compound degrading capacities to gradually developing in the media, therefore providing relatively stable OMP removal during long-term operation.

Among the studied OMPs, biodegradation is considered to be the main removal mechanism for the removal of hydrophilic compounds such as DBP as also reported in Qi et al. (2018). According to our results, DEP, DBP, 2,6-DTBP, and BHT were found removed at higher level than DEHP. Similar observation was reported in Tang et al. (2015). The OMP removals are influenced by physicochemical properties of compounds (Table S1). The compounds having shorter alkyl-side chains (more hydrophilic) are generally highly biodegraded while those having longer chains (hydrophobic) are less susceptible to biodegradation. DEHP has relatively low water solubility and high octanol-water partition coefficients ($\log K_{ow}$ 7.5), therefore tend to adsorb and accumulate at higher extent in the media (Tang et al. 2015). The results has demonstrated that S:C:Fe material could effectively remove OMPs and appeared to be the most efficient CW media in this study.

The presence of plants in the CWs improved the OMP removal by 4.3–17.5%. It helped transport oxygen to the rhizosphere and form micro-aerobic zones that benefit the growth aerobic microorganisms. During the column operation, it was found that DO level in the media was 0.3–0.8 mg/l during unplanted condition. There was no significant difference in DO among different CW media used. When the cattail was introduced, DO was increased to 1.3–3.4 mg/l. This promotion of aerobic condition could promote the biodegradation of OMPs such as phenolic compounds (Dan et al. 2017) and PAEs (Tang et al. 2015). Toyama et al. (2011) also reported that the reed root exudates containing phenolic compounds can support the growth of benzo (a) pyrene-degrading bacterium and induce its degrading activity. The role of plants in CWs is not only providing oxygen transfer but also enhancing abundance and diversity of microorganisms in the rhizosphere by increasing available surface area for bacterial attachment and growth (Wang et al. 2016).

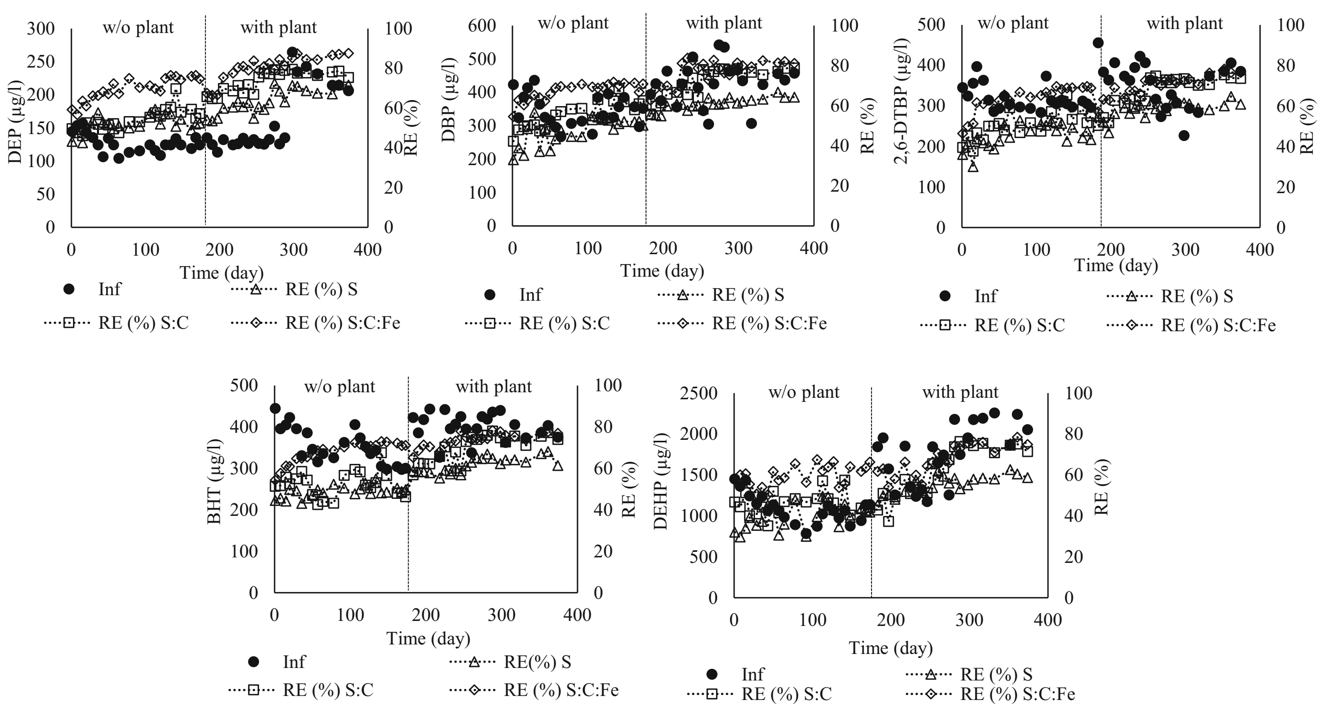

Fig. 2 Influent concentrations and removal efficiencies of OMPs in CW columns during long-term operation

Pollutant accumulation and plant growth

During the column experiment (373 days), carbon content of the media was found increased from 0.42%, 2.26%, and 1.23% to 0.70%, 2.68%, and 2.39% in S, S:C, and S:C:Fe columns respectively. Meanwhile, their nitrogen contents were increasing from 0.06%, 0.06%, and 0.08% to 0.15%, 0.15%, and 0.12%. These results suggest that a part of C and N loaded into the system was accumulated in the media. Among them, sand media had the lowest C and N content and the lowest accumulation. The S:C:Fe media had lower C content compared to S:C media due to the presence of iron powder but its C content became higher at the end of experiment suggesting that there was significant accumulation of organic compounds in the S:C:Fe media. However, N accumulation in the experimental columns was not significantly different. Figure 3 shows the mass removal of OMPs through accumulation in media/plant and biodegradation. Among them, only DEHP was found significantly adsorbed in the system at 32.5%, 44.2%, and 58.4%, in S, S:C, and S:C:Fe media, respectively. The contribution of their removals via plant uptake (accumulation in plant) only accounted for 2.2–3.4%. As for BHT, the removal via plant was 3.3–4.2%. DEP was the most effective compound removed through biodegradation of 62.7%, 70.9%, and 75.5% in S, S:C, and S:C:Fe media followed by DBP and 2,6-DTBP, respectively. High accumulation of DEHP took place due to its hydrophobicity as compared to other studied compounds. The accumulation of pollutants and biomass in the media also led to its decrease hydraulic permeability to $3.24*10^{-5}$, $2.10*10^{-5}$, and $2.75*10^{-5}$ cm/s in S, S:C, and S:C:Fe media respectively.

During long-term operation of CW columns, the growth of cattail was also monitored. The experimental period, the cattail was grown without being harvested. There was no significantly difference ($p > 0.05$) in the growth of cattail among the experimental columns. The density, height, and dry weight of cattail increased by 3–4-folds. The estimated RGR in the experiment was 0.01 per day, which was in the same range as those reported for cattail in CWs treating landfill leachate of 0.02 per day at real tropical landfill (Ogata et al. 2015). From these results, the presence of iron powder in CW media did not have negative impact on plant growth which was in agreement with our previous observation (Chiemchaisri et al. 2015).

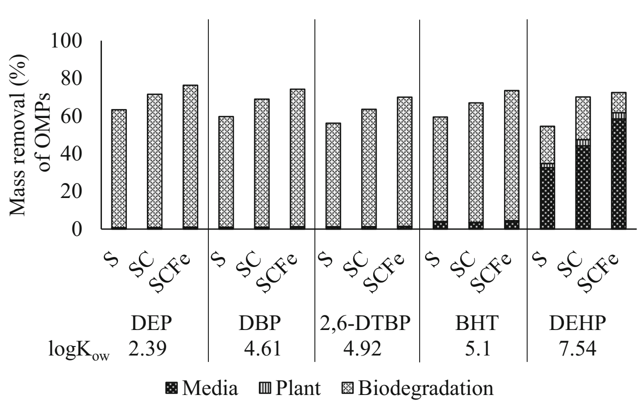

Fig. 3 Mass removal percentages of OMPs from adsorption (to media/plant) and biodegradation in CW columns during long-term operation

OMP adsorption and biodegradation capacities of CW media

The removal mechanisms of OMPs in CW media were confirmed in batch experiments. Their removals via adsorption and biodegradation were quantified using active and inactive media obtained from the experimental columns on the first (day 0) and last days (day 373) of long-term column experiment. The original S:C:Fe media was found to have the highest total removal capacities of OMPs, i.e., DEP, DBP, 2,6-DTBP, BHT, and DEHP at 6.7, 30.3, 15.8, 19.6, and 138.6 μg/g media among the three media examined (Table 3). They were 27–68% and 3–18% higher than those of S media and S:C media respectively. For most OMPs except DEP, adsorption was the major mechanism responsible for OMP removal at day 0. The adsorption of organic substances depends on the size of their molecules, chemical structure, and polarity (Julinová and Slavík 2012). The contribution of adsorptive removal accounted for 60.7–94.4% in the media depending on the hydrophobicity characteristic of OMPs. The highest adsorptive removal was observed for DEHP contributing to 79.4–94.4% in the total removal. For the most hydrophilic compound (DEP), the biodegradation was responsible for 53.2–71.6% in their total removals.

When the media became matured at the end of experiment (day 373), total OMP removal capacities were found increasing to 1.09–2.23-folds of the initial capacities. For this matured media, the highest removal capacities of DEP, DBP, 2,6-DTBP, BHT, and DEHP were observed for S:C:Fe media at 12.6, 46.9, 25.4, 32.6, and 150.5 μg/g media (Table 3). However, the most notable increase in total removal capacities was observed for S media (1.68–2.23-folds). Among the studied OMPs, the highest improvement removal capacities were observed for DEP as the biodegradation capacities of media were developed along the experimental period. Understandably, the least improvement (less than 10%) was observed in case of DEHP especially in S:C and S:C:Fe media as the adsorption was mainly responsible in its removal at 63.5 and 67.4% respectively .

Kinetics of OMP removal in CW media

The kinetic parameters for OMP removal through adsorption and biodegradation were derived. During the determination of

Table 3 Adsorption and biodegradation capacities (μg/g) of different CW media

Compounds	Adsorption			Biodegradation			Total		
	S media	S:C media	S:C:Fe media	S media	S:C media	S:C:Fe media	S media	S:C media	S:C:Fe media
0 days									
DEP	2.2	2.9	1.9	2.5	3.6	4.8	4.7	6.5	6.7
DBP	12.2	15.5	18.7	7.9	9.3	11.6	20.1	24.8	30.3
2,6-DTBP	7.4	9.0	10.2	3.7	4.6	5.6	11.1	13.6	15.8
BHT	10.3	12.2	14.5	4.1	5.1	7.2	14.4	17.3	19.6
DEHP	35.5	101.0	130.8	9.2	13.8	7.8	44.7	114.8	138.6
373 days									
DEP	2.1	1.9	2.7	8.4	9.3	9.9	10.5	11.2	12.6
DBP	7.8	10.6	9.4	27.6	30.3	37.5	35.4	40.9	46.9
2,6-DTBP	5.1	7.3	8.2	13.6	16.2	17.2	18.7	23.5	25.4
BHT	9.1	9.4	11.5	17.0	20.6	21.1	26.1	30.0	32.6
DEHP	27.4	79.7	101.5	64.3	45.8	49.0	91.7	125.5	150.5

adsorption kinetics, the data was found best fitted to pseudo-second-order (PSO) model as shown in Eq. 6.

$$\frac{dqt}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

Where q_e (μg/g) is the solid phase concentration of the OMPs at equilibrium, q_t (μg/l) is the solid phase concentration at contact time *t*, and k_2 (g/μg/h) is the rate constant.

The kinetics of OMP biodegradation were described by first-order model. The rate constant of OMP removal via biodegradation was obtained from the following equation:

$$\ln\left(\frac{q_t}{q_0}\right) = -k_t t \quad (7)$$

Where q_0 (μg/l) and q_t (μg/l) are the concentrations of contaminants in aqueous solution at an initial time and time *t* (h). k_t (h^{-1}) is the first-order rate constant for the removal of the contaminants.

The kinetic plots of OMP concentrations during batch experiments are shown in the supplement (Fig. S3-S4) with the derived kinetic parameters shown in Table 4. For adsorption, the kinetic expression could be explained as pseudo-second-order with solid phase concentration at equilibrium (q_e) and rate constant (k_2) determined. On initial day, q_e was found highest for DEHP at 37.3, 104.2, and 137 μg/g for S, S:C, and S:C:Fe media whereas they were much lower (2.2–18.2 μg/g) for other compounds. The k_2 constant for DEHP was also higher, being 2.17–6.39 times of those of other compounds. As the media became matured, most of adsorption kinetic parameters decreased except those of DEP in S and S:C:Fe media. These results suggested that the adsorption removal of OMPs decreased with time except DEP which

Table 4 Kinetic parameters of adsorption and biodegradation of OMPs in media

Compounds	Adsorption (PSO)						Biodegradation (first-order)		
	S media		S:C media		S:C:Fe media		S media	S:C media	S:C:Fe media
	q_e (μg/g)	k_2 (g/μg/h)	q_e (μg/g)	k_2 (g/μg/h)	q_e (μg/g)	k_2 (g/μg/h)	k (h^{-1})	k (h^{-1})	k (h^{-1})
0 days									
DEP	2.5	0.041	3.1	0.044	2.2	0.033	0.008	0.012	0.017
DBP	15.6	0.070	15.6	0.079	18.2	0.097	0.006	0.007	0.009
2,6-DTBP	7.6	0.054	9.3	0.068	10.5	0.080	0.005	0.006	0.008
BHT	10.9	0.061	12.9	0.069	15.0	0.088	0.005	0.006	0.008
DEHP	37.3	0.162	104.2	0.189	137.0	0.211	0.002	0.003	0.002
373 days									
DEP	2.9	0.050	2.0	0.038	3.0	0.041	0.037	0.046	0.051
DBP	9.0	0.055	11.3	0.068	10.0	0.076	0.028	0.032	0.046
2,6-DTBP	5.4	0.052	7.5	0.055	8.4	0.070	0.026	0.032	0.036
BHT	9.4	0.054	9.7	0.063	12.3	0.080	0.026	0.032	0.036
DEHP	28.0	0.091	85.5	0.145	106.4	0.169	0.017	0.009	0.010

The kinetic parameters were averaged from triplicate experiments biodegradation is its major removal pathway. The obtained kinetic values from this study were found in the same range as those reported for adsorption of phthalate esters on marine sediments (Mohammadian et al. 2016); however, the q_e values were much lower than reported value for phthalate esters adsorbed to clay soil (Liu et al. 2013) due to the presence of other organic substances in landfill leachate in this study.

The biodegradation kinetics of OMPs followed first-order expression (Wen et al. 2014). Most of the derived kinetic rate constant (k) were found low (0.002–0.017 h^{-1}) in all media at day 0. However, they were substantially increased by 3–8.5-folds during the long-term CW operation. The highest biodegradation rates of OMPs were observed in S:C:Fe media except that of DEHP which was found less than S media but all of them was found at relatively low value (0.009–0.017 h^{-1}). These results suggested significant improvement of OMP biodegradation in CW media over time. The results obtained from this study have demonstrated that the removal of OMPs from landfill leachate in CW containing reactive media could be sustained during long-term operation due to the development of biodegradation capacities of microorganisms attached on the media. The incorporation of clay and iron powder into the media helps promote adsorption of OMPs through increasing the surface area of the media while allowing microbial attachment and growth to promote their biodegradation capacities which also gradually developed during long-term operation.

Conclusion

Introduction of clay and iron power into CW media significantly enhanced the removals of organics (BOD, COD), nitrogen (NH_3, TKN), and OMPs (phenolic compounds, PAEs). Long-term operation (373 days) of experimental CW column containing reactive media (sand 60%, clay 30%, iron powder 10%, w/w) yielded satisfied and sustainable treatment of landfill leachate. Majority of the studied OMPs (2,6 DTBP, BHT, DEP, DBP) was removed through biodegradation except DEHP which were found adsorbed and accumulated in the CW media. The presence of vegetation (Cattail) helped improve pollutant removal through increase of oxygen transfer into plant root zone. The removals of OMPs in CW media were verified through batch experiments and the results suggested adsorption (pseudo-second-order kinetics) and biodegradation (first-order kinetics) as the main mechanisms responsible for their removals. Both adsorptive and microbial removals were enhanced by the presence of clay and iron powder materials in the CW media.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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