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Technical note

Removal efficiencies of constructed wetland and efficacy of plant on treating benzene

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A B S T R A C T

Leaking underground petroleum storage poses human and environmental health risks as it contaminates the soil and the groundwater. Of the many contaminants, benzene – a major constituent of gasoline, is of primary concern. It is an identified carcinogen with a permissible limit set at a low level of 0.005 mg L^{-1}. This poses technical and regulatory challenge to remediation of contaminated sites. Various specialized treatment methods are available, but despite of the high removal efficiencies of sophisticated treatments, the residual level still poses health risks. Thus, additional alternative ways that are cost effective and require minimum technical expertise are necessary, and a constructed wetland (CW) is a potential alternative. This study evaluates the performance of a surface flow type CW for the removal of benzene from the contaminated water. It further determines the efficacy of a common reed plant *Phragmites karka* in treating benzene. Planted and unplanted CW were acclimated with benzene for 16 wk and tested for an 8-d hydraulic retention time at benzene levels of 66 and 45 mg L^{-1}. Results indicate that the planted CW performed better and gave reliable and stable results.

1. Introduction

Constructed wetlands (CWs) have been used to treat wastewater for the removal of a wide variety of contaminants, such as suspended solids, organic compounds, nutrients, pathogens, metals, and emerging contaminants [1–7]. Aside from its effectiveness in pollutant removal, it has also displayed cost efficiency in wastewater treatment [3,8,9].

Of the several removal mechanisms involved in the operation of CWs: sedimentation, filtration, volatilization, adsorption, plant uptake, and bacterial activity [10] with bacterial activity often playing the most important role in removing contaminants [11,12]. And though plant uptake is a minor contributory factor for contaminant removal [13], plants significantly improve bacterial activities [13–15] as its rhizosphere provides the area for microbes to grow, its root exudates provide nutrients that support microbial growth [11,12], and its roots supply oxygen needed by aerobic bacteria [16].

A number of studies have investigated the effect of plants in treating organic pollutants [17–19]. *Phragmites australis* significantly enhanced the capacity of a pilot scale horizontal subsurface flow CW in removing monochlorobenzene and perchloroethylene [17]. A significant difference was also observed in the performance of planted and unplanted CW in terms of nutrient removal [18]. However, despite the improved nutrient removal, no significant difference was found in organic matter removal between planted and unplanted CW. This is attributed to the sole or major dependence of organic compound degradation on the microbial systems in the soil [15].

Despite the number of studies dealing with benzene removal by CWs [20–24], little attention has been given to determining the efficacy of plant on treating benzene and the optimal hydraulic retention time (HRT) for benzene treatment by CWs. These specific concerns will be addressed in this study using a surface flow type CW and *Phragmites karka* as the vegetation. CW efficiency was analyzed at benzene levels of 66 and 45 mg L^{-1}.

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2. Materials and methods

The experimental set-up consists of two horizontal surface flow CWs. Containers with fiberglass walls and steel reinforcements measuring 1 m long, 0.6 m wide, and 0.8 m high were used. The solid media consist of local materials from Vietnam. The lower 0.1 m layer is made of gravel (2–3.15 mm grain size) and topped with soil (sand and silt) to a height of 0.3 m. The water level was maintained at a height of 0.1 m above the solid media.

One CW was planted with local common reed *P. karka* at a density of 0.44 rhizomes m^{-2} [25] while the other served as the control and contains only the solid media. *P. karka* was used since it is the type available locally and the potential to treat organic contaminant in *Phragmites* – planted CW has been described in literature [7,17,18,26,27]. The CW water is a BH medium [28] (containing 9in g L^{-1}) 0.2 $MgSO_4 \cdot 7H_2O$, 0.02 $CaCl_2$, 1 KH_2PO_4, 1 K_2HPO_4, 1 NH_4NO_3, and 0.05 $FeCl_3$. The acclimation process involved spiking of the water with 100 mg L^{-1} of benzene weekly for 16 wk to encourage the growth of benzene-degrading bacteria.

Optimal HRT was determined by treating synthetic wastewater (66 mg L^{-1} of benzene in distilled water) in the CW. This concentration was employed in order to preclude inhibitory conditions that affect bacteria as observed at higher concentration and elicit improved contaminant biodegradation commonly observed at concentration lower than 100 mg L^{-1} [29,30]. Benzene removals in the effluent samples from the planted CW at four different HRTs (2, 4, 6, and 8 d) were determined. Optimal HRT is selected and used for the succeeding experiments.

In the actual experimental runs, both systems were fed with synthetic wastewater at the optimal HRT achieved above and at benzene concentrations of 66 mg L^{-1} and another concentration of 45 mg L^{-1} to provide comparison. Effluent samples were taken every day for 3–7 d. Fig. 1 shows a photograph of the actual set-up.

Each effluent sample underwent solvent extraction using hexane to extract benzene. A calibration curve was generated from the extraction and analysis of the standard solutions made by preparing several solutions of benzene at known concentrations. Analyses of actual effluent samples were done by Gas Chromatography with Flame Ionization Detector (GC-FID), and concentrations were determined by comparing with the calibration curve generated. Each of the steps is elaborated in the following paragraphs.

For benzene extraction, 4 mL hexane was added to 50 mL of the collected effluent. The solution was shaken at 120 rpm for 20 min at room temperature to enable effective extraction of the benzene to hexane. The solution is then allowed to stand undisturbed until two distinct layers were formed. One mL of the upper layer solution is suctioned by a syringe and transferred to vials. The samples were securely covered and stored at 4 °C to prevent volatilization of benzene.

The calibration curve was prepared through this procedure. Measured amounts of benzene were spiked in distilled water to achieve concentrations of 10–90 mg L^{-1}. Each of these solutions underwent benzene extraction process as described previously. Analysis with GC-FID gave peak areas that correlated with concentration. A calibration curve constructed from these six benzene levels was used as the basis for the computation of benzene concentrations of the effluent samples tested with the GC-FID method.

The GC used (7890A-Agilent, USA) was fitted with an Agilent HP-5MS 30 m × 0.25 mm × 0.25 μm capillary column and equipped with a FID (6890N-Agilent, USA). Oven, injector, and detector temperatures were 280, 300, and 280 °C respectively. Nitrogen gas was used as the carrier gas.

Fig. 1. Surface flow constructed wetland set-up.

3. Results and discussion

3.1. Optimal HRT

Fig. 2 summarizes the results of the optimal HRT tests. It is apparent that the treatment efficiency increases with HRT. The same relation was observed in other studies as effluent concentrations increase with loading; however, increasing the HRT higher than 8 d does not result in a significant increase in efficiency anymore [31,32] and will require large-sized CWs. Thus, an HRT of 8 d was used in all test runs in this study.

3.2. Benzene removal efficiency

Fig. 3 shows the benzene removal efficiency with planted and unplanted CW at the feed benzene concentration of 66 mg L^{-1}. Results suggest that while planted CW achieved removals at an average of 48%, the unplanted CW resulted only to around 31% efficiency. This removal efficiency may be lower than that observed in literature [20–24] mainly due to the significantly lower benzene concentrations used in this study. This demonstrates a significant difference of 17% between the treatment efficiencies of the planted and unplanted CW.

The 17% increase in the benzene removal for the planted CW demonstrates that *P. karka* caused the significant enhancement in removal. This could be attributed to the capacity of plants to release

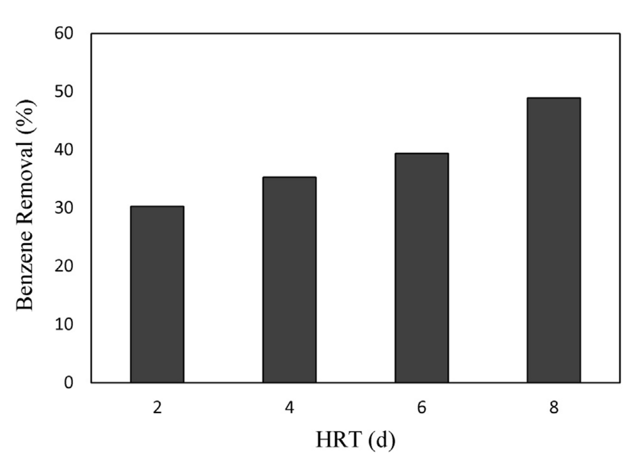

Fig. 2. Benzene removal at various HRT.

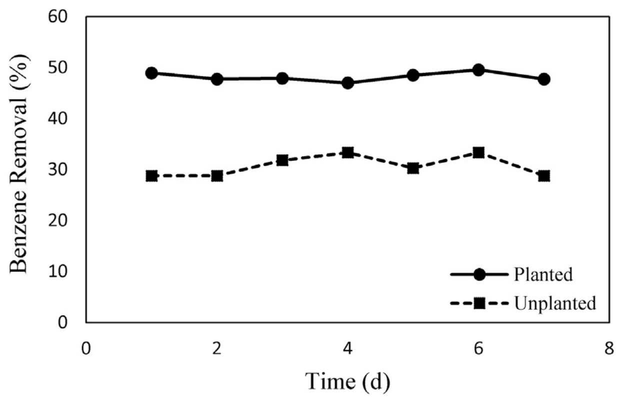

Fig. 3. Removal of benzene in planted and unplanted surface flow constructed wetland at 8 d HRT.

oxygen to rhizospheres [16]. The abundance of oxygen supports the growth of aerobic bacteria which can consume and degrade benzene [33]. As a result, the rate of benzene removal can increase significantly. *P. karka* could further enhance bacterial growth by providing the surface area and nutrients through its root exudates [11,12]. Another possible pathway of benzene removal is through uptake, as studies prove that plants are also able to uptake contaminants [9,18,26].

Another experiment was performed to test the performance of the CW system at a lower benzene concentration of 45 mg L^{-1}. The results gave almost complete removals with effluent concentration at an average of 0.03 mg L^{-1}. This demonstrates that the treatment efficiency of the system is better at the lower benzene concentration. At 66 mg L^{-1}, lower efficiency is attributed to lower utilization rates at higher concentrations [34] or to the toxic and inhibitory effect of high benzene levels on bacterial growth [29]. Although this concentration is lower than the reported level that no inhibition occurs [30], this variation is attributable to the difference in the microbial system developed in different set-ups.

4. Conclusions

This study demonstrated the effectiveness of a surface flow CW in removing benzene from wastewater and the improvement of efficiency in the planted CW system. The presence of *P. karka* has enhanced benzene removal from the 66 mg L^{-1} influent benzene wastewater concentration by 17% at an 8-d HRT. The planted CW system exhibited excellent and nearly complete removals at an influent concentration level of 45 mg L^{-1}, suggesting that toxic and inhibitory effects are system-dependent and that these effects are absent for this particular system at this contaminant level.

The use of local media and common vegetation in this CW system indicates the ease of construction and economic advantage of this treatment technology. Since CW requires minimal operational control and technical expertise, this method is a suitable alternative treatment for high benzene concentration wastewater or as an additional treatment method to supplement existing treatments prior to disposal to the environment. The latter application necessitates testing CW system at lower concentrations equivalent to the benzene effluent concentrations of the existing treatment facilities and using more sensitive quantitative analytical instruments. To further understand the mechanism of the enhanced removal in the presence of *P. karka*, isolation, identification, and analysis of the growth of indigenous bacteria growing in this system is imperative. In addition, analysis of plant uptake at different plant parts is also worthwhile.

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References

[1] Goulet RR, Pick FR, Droste RL. Test of the first-order removal model for metal retention in a young constructed wetland. Eco Eng 2001;17:357–71.
[2] Green MB, Griffin P, Seabridge JK, Dhobie D. Removal of bacteria in subsurface flow wetlands. Water Sci Technol 1997;35:109–16.
[3] Kadlec RH, Wallace S. Treatment Wetlands. 2nd ed. Boca Raton, FL: CRC Press; 2008.
[4] Matamoros V, Bayona JM. Elimination of pharmaceuticals and personal care products in subsurface flow constructed wetlands. Environ Sci Technol 2006;40:5811–6.
[5] Ranieri E, Gikas P, Tchobanoglous G. BTEX removal in pilot-scale horizontal subsurface flow constructed wetlands. Desalin Water Treat 2013;51:3032–9.
[6] Ranieri E, Verlicchi P, Young TM. Paracetamol removal in subsurface flow constructed wetlands. J Hydrol 2011;404:130–5.
[7] Zhang DQ, Gersberg RM, Ng WJ, Tan SK. Removal of pharmaceuticals and personal care products in aquatic plant-based systems: a review. Environ Pollut 2014;184:620–39.
[8] Langergraber G. Are constructed treatment wetlands sustainable sanitation solutions? Water Sci Technol 2013;67:2133–40.
[9] Vymazal J. Constructed wetlands for treatment of industrial wastewaters: a review. Eco Eng 2014;73:724–51.
[10] Chazarenc F, Gagnon V, Comeau Y, Brisson J. Effect of plant and artificial aeration on solids accumulation and biological activities in constructed wetlands. Eco Eng 2009;35:1005–10.
[11] Tanner CC. Plants as ecosystem engineers in subsurface-flow treatment wetlands. Water Sci Technol 2001;44:9–17.
[12] Vymazal J, Kropfelova L. Removal of organics in constructed wetlands with horizontal sub-surface flow: a review of the field experience. Sci Total Environ 2009;407:3911–22.
[13] Stottmeister U, Wiessner A, Kuschk P, Kappelmeyer U, Kastner M, Bederski O, et al. Effects of plants and microorganisms in constructed wetlands for wastewater treatment. Biotechnol Adv 2003;22:93–117.
[14] Faulwetter JL, Gagnon V, Sundberg C, Chazarenc F, Burr MD, Brisson J, et al. Microbial processes influencing performance of treatment wetlands: a review. Ecol Eng 2009;35:987–1004.
[15] Yang Q, Chen ZH, Zhao JG, Gu BH. Contaminant removal of domestic wastewater by constructed wetlands: effects of plant species. J Integr Plant Biol 2007;49:437–46.
[16] Tanner CC, Kadlec RH, Gibbs MM, Sukias JPS, Nguyen ML. Nitrogen processing gradients in subsurface-flow treatment wetlands – influence of wastewater characteristics. Ecol Eng 2002;18:499–520.
[17] Chen ZB, Wu SB, Braeckevelt M, Paschke H, Kastner M, Moser H, et al. Effect of vegetation in pilot-scale horizontal subsurface flow constructed wetlands treating sulphate rich groundwater contaminated with a low and high chlorinated hydrocarbon. Chemosphere 2012;89:724–31.
[18] Kyambadde J, Kansiime F, Gumaelius L, Dalhammar G. A comparative study of Cyperus papyrus and Miscanthidium violaceum-based constructed wetlands for wastewater treatment in a tropical climate. Water Res 2004;38:475–85.
[19] Seeger EM, Kuschk P, Fazekas H, Grathwohl P, Kaestner M. Bioremediation of benzene-, MTBE- and ammonia-contaminated groundwater with pilot-scale constructed wetlands. Environ Pollut 2011;159:3769–76.
[20] Tang XQ, Eke PE, Scholz M, Huang SL. Seasonal variability in benzene removal by vertical-flow constructed wetland filters. Water Air Soil Poll 2009;202:259–72.
[21] Eke PE, Scholz M. Benzene removal with vertical-flow constructed treatment wetlands. J Chem Technol Biot 2008;83:55–63.
[22] Rakoczy J, Remy B, Vogt C, Richnow HH. A bench-scale constructed wetland as a model to characterize benzene biodegradation processes in freshwater wetlands. Environ Sci Technol 2011;45:10036–44.
[23] Tang XQ, Eke PE, Scholz M, Huang SL. Processes impacting on benzene removal in vertical-flow constructed wetlands. Bioresour Technol 2009;100:227–34.
[24] Tang XQ, Scholz M, Eke PE, Huang SL. Nutrient removal as a function of benzene supply within vertical-flow constructed wetlands. Environ Technol 2010;31:681–91.
[25] Idris A, Abdullah AGL, Hung YT, Wang LK. Wetlands for wastewater treatment. In: Wang LK, Tay JH, Tay STL, Hung YT, editors. Handbook of Environmental Engineering. Environmental Bioengineering, Vol 11. New York: Humana Press; 2010.
[26] Vymazal J. Emergent plants used in free water surface constructed wetlands: a review. Ecol Eng 2013;61:582–92.
[27] Billore SK, Singh N, Sharma JK, Dass P, Nelson RM. Horizontal subsurface flow gravel bed constructed wetland with *Phragmites karka* in central India. Water Sci Technol 1999;40:163–71.
[28] Lee EY, Hong SH, Oh MH, Lim JS. Characterization biodegradation of benzene, toluene, ethylbenzene, and xylenes by the newly isolated bacterium Pseudomonas putida AY-10 in rhizosphere of wastewater treatment reed. In: 3rd International Conference on Chemical. Singapore: Biological and Environmental Engineering; 2011 Sep 23–25.

[29] Dou JF, Ding AZ, Liu X, Du YC, Deng D, Wang JS. Anaerobic benzene biodegradation by a pure bacterial culture of Bacillus cereus under nitrate reducing conditions. J Environ Sci-China 2010;22:709–15.
[30] Alvarez PJ, Anid PJ, Vogel TM. Kinetics of aerobic biodegradation of benzene and toluene in sandy aquifer material. Biodegradation 1991;2:43–51.
[31] Akratos CS, Tsihrintzis VA. Effect of temperature, HRT, vegetation and porous media on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands. Ecol Eng 2007;29:173–91.
[32] Mayo AW, Mutamba J. Effect of HRT on nitrogen removal in a coupled HRP and unplanted subsurface flow gravel bed constructed wetland. Phys Chem Earth 2004;29:1253–7.
[33] El-Naas MH, Acio JA, El Telib AE. Aerobic biodegradation of BTEX: progresses and prospects. J Environ Chem Eng 2014;2:1104–22.
[34] Schirmer M, Butler BJ, Roy JW, Frind EO, Barker JF. A relative-least-squares technique to determine unique Monod kinetic parameters of BTEX compounds using batch experiments. J Contam Hydrol 1999;37:69–86.