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Water depths and treatment performance of pilot-scale free water surface constructed wetland treatment systems for simulated fresh oilfield produced water

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ABSTRACT

Water depth may enhance performance of constructed wetland treatment systems (CWTSs) for renovation of complex mixtures such as fresh oilfield produced waters (FOPWs) that contain constituents such as oil and divalent metals (i.e. Cd, Cu, Ni, and Zn). The purpose of this research was to evaluate the influence of water depth on treatment performance of a free water surface pilot-scale CWTS for renovating simulated FOPW. A CWTS was designed with an oil-water separator and wetland cells with fixed hydraulic retention time (HRT), surface area, volume, water depth, hydraulic loading rate (HLR), and mass loading rate (MLR) as treatment variables. Replicated wetland series were constructed with different water depths and four cells for each series. For wetland series with water depths of 15 and 23 cm, rates of removal of oil marker compounds $(0.44-1.17 \text{ day}^{-1})$ were greater than rates of removal for wetland series with water depths of 46 and 56 cm (no removal-0.12 day⁻¹). As water depth decreased (i.e. from 56 to 15 cm) and sediment redox potential increased (i.e. from -250 to 234 mV) in the wetland series, concentrations of oil marker compounds decreased in outflows of the wetland cells. For wetland series with water depths of 46 and 56 cm, rates of removal for Cd, Cu, Ni, and Zn $(0.31-1.11 \text{ day}^{-1})$ were greater than rates of removal for wetland series with water depths of 15 and 23 cm $(0.003 \text{ and } 0.23 \text{ day}^{-1})$. As water depth increased (i.e. from 15 to 56 cm) and sediment redox potential decreased in the wetland series, Cd, Cu, Ni, and Zn concentrations decreased in outflows of the wetland cells. From these results, water depth either enhanced or decreased treatment performance of a CWTS depending on the targeted constituent (i.e. oil, Cd, Cu, Ni, and Zn) due to changes in the sediment redox potential and dissolved oxygen content in the wetland cells. Data from this study indicated that sequential wetland cells could enhance the treatment of complex mixtures like FOPW by establishing specific conditions in each wetland cell targeting removal of different classes of constituents.

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1. Introduction

Constructed wetland treatment systems (CWTSs) may be a viable option for renovation of complex mixtures like produced waters containing constituents such as oil and divalent metals (Knight et al., 1999; Ji et al., 2002; Murray-Gulde et al., 2003; Ji et al., 2007). Given the limited supply of fresh water in the United States, renovation of produced waters such as fresh oil-field produced waters (FOPWs; ≤5000 mg Cl/L; Wetzel, 2001) may assist with fresh water supplies in areas with limited resources (Nijhawan and Myers, 2006). Since FOPWs often contain a variety

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of constituents that must be treated prior to use for serviceable purposes, constructed wetlands for renovation of these waters must be designed for effective and efficient performance and design parameters such as water depth may enhance the treatment performance that can be achieved with a given "footprint" or size of a CWTS. This research investigated the influence of a series of water depths on the performance of pilot-scale constructed wetlands for treatment of simulated FOPW containing oil and divalent metals.

Water depth may directly or indirectly affect treatment performance (i.e. rates and extents of removal of targeted constituents) of a constructed wetland. Previous studies have investigated water depth and treatment performance for a variety of impaired waters such as domestic wastewater and industrial waters in subsurface flow (García et al., 2004, 2005; Headley et al., 2005; Matamoros







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et al., 2005) and free water surface (FWS) CWTSs (Stark et al., 1996; Gillespie et al., 2000). For this study, we focused on FWS systems because they are less expensive to construct than many subsurface systems (Fountoulakis et al., 2009) and they are more readily constructed in remote areas. There are at least two potential experimental designs for evaluation of water depth and treatment performance in FWS CWTS. The principal differences in these designs are fixed vs. variable surface area, hydraulic retention time (HRT), and volume as well as the sediments and plants used. If water depth is the experimental parameter of interest and we examine the influence of a series of water depths on treatment performance, then decisions must be made regarding inflow concentrations of targeted constituents for treatment, hydraulic loading rate (HLR), mass loading rate (MLR), HRT, surface area, and volume of the FWS CWTS as well as the compatibility of plants with the selected water depths. For purposes of this study, we used an experimental design with fixed surface area, inflow concentrations, and HRT, and water depth, HLR, and MLR as treatment variables. With a fixed surface area in the pilot-scale wetland cells, some parameters are directly related to water depth such as net oxygen supply rate (NOSR) and the volume of water in a wetland cell (Kadlec and Knight, 1996). However, parameters such as sediment redox potential are indirectly related to water depth since it is affected by changes in the NOSR and sediment oxygen demand (SOD; Hargrave, 1972) as well as radial oxygen loss by emergent vegetation (Brix, 1997; Vretare et al., 2001). Controlling much of the oxygen supply to the sediment, water depth in a FWS constructed wetland can affect the prevalent redox conditions by producing or failing to produce a sufficient barrier between the sediment and atmosphere (Kadlec and Knight, 1996). By altering the bulk sediment redox potential in a wetland, water depth can indirectly affect removal pathways and processes [i.e. precipitation of metals by sulfides produced by dissimilatory sulfate reduction (-100 to -250 mV; Faulwetter et al., 2009) and biodegradation (Rodgers and Castle, 2008) of oil $(\geq 100 \text{ mV})$ in a CWTS]. We hypothesized that the performance of these pilot-scale CWTSs for treating simulated FOPW containing oil would be inversely related to water depth, while removal rates for Cd. Cu. Ni. and Zn would be positively related to water depth. In constructed wetlands, removal rates for each constituent of interest may change due to different sediment conditions (Faulwetter et al., 2009) in the wetland cells.

Interest in the use of CWTSs for renovation of produced waters such as FOPWs provided an opportunity to test some hypotheses regarding design parameters affecting treatment performance related to water depth. FOPWs are generated by extraction, refining, and processing of oil from many basins of the United States (e.g. Green River; Powder River; Gulf Coast; Permian) and contain constituents such as oil and Cd, Cu, Ni, and Zn (USGS, 2006; Fakhru'l-Razi et al., 2009) that must be treated prior to use for beneficial purposes. One approach for designing wetlands involves consideration of constituent removal that is strongly dependent on HLR and influent concentrations and to a lesser extent on water depth, internal plant communities, and hydraulic efficiency [i.e. ability of a constructed wetland to distribute inflow waters evenly in a cell (Persson, 2000); Knight et al., 1999]. For wetland systems, operative pathways and processes in a wetland cell depend specifically on sediment redox conditions that can be influenced by water depth. For example, deeper water depths (~0.6 m; Sorrell et al., 2002) may decrease the NOSR contributing to an anaerobic environment in a wetland cell and diminished rates of removal of some pharmaceuticals (Matamoros et al., 2005) and other organics such as oil. Depending on the design of a CWTS, HLRs within a reasonable range may or may not influence a system's performance. Another general concept for designing FWS wetlands posits that the volumetric based first-order rate coefficient (day⁻¹) and water depth

Table 1

Simulated FOPW composition in 3780 L of municipal water in a polypropylene tank (reservoir).

ass
g
g
g
g
0 g

are inversely related, while the area-based first-order rate coefficient (cm/day) is hypothetically constant with changes in water depth (Kadlec and Knight, 1996; Knight et al., 1999). However, when water depth and area-based removal rates are increased, the removal rates for specific metals may increase, but the removal rates for oil may decrease in wetland systems. Some researchers have suggested that metal removal efficiencies are highly correlated with MLRs and influent concentrations (Stark et al., 1995; Kadlec and Knight, 1996; Knight et al., 1999). For this study, MLRs increased with water depths, however, conditions prevalent in the wetland cells with lower MLRs may or may not be conducive to metal removal.

The purpose of this research was to evaluate influences of a series of water depths on treatment performance of FWS pilot-scale CWTSs for renovating simulated FOPW. Specific objectives of this study were to: 1) prepare simulated FOPW, 2) design and construct the pilot-scale CWTSs, 3) compare treatment performance data (i.e. rates, extents, and efficiencies of removal of oil, Cd, Cu, Ni, and Zn) for the pilot-scale CWTSs at five water depths (i.e. 15, 23, 33, 46, and 56 cm), and 4) determine the effects of mass loading rates on sediment redox potential and sediment organic matter content in the wetland series.

2. Materials and methods

2.1. Formulation of simulated fresh oilfield produced water

Simulated FOPW was formulated based on constituent concentrations in FOPWs reported in peer-reviewed literature (i.e. Alley et al., 2011) and government documents (i.e. USGS, 2006) as well as analyses of PW samples (n=3) sent by colleagues from Gulf Coast oilfields in the continental United States. Oil and grease concentrations in PW samples were measured using USEPA method 1664b, and metals were measured using Inductively Coupled Plasma-Optical Emission Spectrometry (APHA, 2005). Ions in FOPW samples were measured using ion chromatography (Dionex LC20 Chromatograph; APHA, 2005). An ionic balance was calculated [i.e. Σ cations (meq/L)+ Σ anions (meq/L)] from analyte concentrations to formulate simulated FOPW with appropriate salts to accurately achieve ionic composition and strength as well as salinity and hardness. The oil component for the simulated FOPW formulation was conventional light oil (Rotella® T 15W40), a costeffective and reproducible alternative to using an actual crude oil. General water characteristics (i.e. pH, dissolved oxygen, conductivity, alkalinity, and hardness; APHA, 2005) were also measured. Simulated FOPW was composed of oil, Cd, Cu, Ni, Zn, and salts well-mixed with 3780L of municipal water in a polypropylene tank (reservoir; Table 1). The simulated FOPW reservoir provided pilot-scale systems with water for approximately six days prior to refilling. This formulation of FOPW resulted in the following concentrations of constituents of interest targeted for treatment: 6 mg Cd⁺²/L, 4 mg Cu⁺²/L, 6 mg Ni⁺²/L, 6 mg Zn⁺²/L, and 100 mg Rotella[®] T 15W40/L.

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