Potential Role of Constructed Wetlands for Treatment of Pharmaceuticals and Personal Care Products in Wastewater

by Douglas J. Daley and Lacey N. Kucerak

The purpose of this article is to introduce opportunities to treat contaminants of emerging concern (CECs) in wastewater effluent using constructed wetlands. CECs are a broad category of synthetic compounds that are increasingly prevalent in wastewater, such as pharmaceuticals and personal care products (PPCPs) or endocrine disrupting compounds (EDCs) (USEPA 2010). Concern regarding CECs has been driving an increasing amount of research over the past decade about the effect of these contaminants on the aquatic environment (Jones et al. 2005; Kolpin et al. 2002) and alternative treatments. Potential adverse impacts of CECs in aquatic systems include feminizing aquatic animals (endocrine disruptors), developing resistance among human pathogens (antibiotics) or inducing toxic responses in aquatic organisms (Huber et al. 2005). Due to their widespread use, CECs enter the water environment in developed countries largely through wastewater treatment plant (WWTP) effluent. While conventional activated sludge facilities were designed to treat moderate levels of readily biodegradable carbon compounds, removal effectiveness of PPCPs in WWTPs varies greatly because of the wide range of chemical, biological and physical properties (Verlicchi 2012) as well as the wide range of influent concentrations that range across six orders of magnitude from 0.1 to 10^5 ng L^-1 (Oulton et al. 2010).

Highlighted here is recent research being conducted to take advantage of the sorption and oxidation potential of constructed treatment wetlands. Wetland treatment provides opportunities for both small and large WWTPs, either as a stand-alone process or as a polishing step following both conventional and advanced treatment technologies. Research paper citations are provided for those readers interested in gathering specific details or further investigating the feasibility of wetland treatment of CECs.

Research in Review

Analysis of opportunities to control or remove CECs from the water environment tends to focus on end-of-pipe treatment systems. Scientific investigations that have focused on the efficacy continued on page 32

A constructed treatment wetland, such as this one, may use any combination of free water surface and submerged flow conditions to provide extended biological and physical treatment of contaminants of emerging concern. Vegetation provides treatment benefits, with secondary ecological benefits of habitat and aesthetic enhancement.
of conventional activated sludge wastewater treatment processes have generally determined that CEC treatment is highly variable—ranging from no effect to completely effective—and depends on the physical and chemical properties of individual contaminants of concern. For example, primary treatment processes have little effect on hydrophilic compounds such as ibuprofen (Zhu 2014). Secondary treatment processes may remove ibuprofen to concentrations that present low risk, yet there is still variability in performance, with detectable concentrations ranging across three orders of magnitude (0.001 μg/L to 4.2 μg/L) (Jones et al. 2003; Zhu 2014). In contrast, treatment of pharmaceuticals such as carbamazepine, an anticonvulsant, in a biological WWTP is largely ineffective, with 38 studies reporting removal rates of less than 30 percent (Gagnon and Lajenness 2012; Oulton et al. 2010).

Investigations into treatment or destruction of CECs in conventional treatment systems tend to focus on which operating conditions could be modified to improve removal effectiveness (e.g., sludge retention time, or SRT). Greater SRTs have been attributed with promoting the development and adaptation of microorganisms to remove xenobiotics, as well as improving treatment effectiveness of sorbed PPCPs through improved solids separation. There appears to be little benefit of increasing SRT beyond 30 days (Verlicchi 2012) and removal of highly soluble compounds is minimal. Rather than focusing solely on removal efficiency, however, one must consider the potential ecological risk associated with PPCPs in both the treated effluent and the excess sludge. Zhu et al. (2014) reports that the predicted no effect concentration (PNEC) of compounds such as sulfamethoxazole is less than 0.5 μg/L in water, and less than 50 μg/kg in sludge. Evaluation of sludge from two WWTPs indicated that sulfamethoxazole presented a “high” risk to the ecological environment, whereas ibuprofen in sludge presented no risk (Zhu et al. 2014).

Other studies focus on the use of advanced treatment technologies (e.g., ozonation, chlorine dioxide) as polishing processes. Chlorine dioxide doses ranging from 8 to 20 mg/L following secondary treatment resulted in effective oxidative degradation of 39 active pharmaceutical ingredients in 18-hour bench-scale experiments. However, removal effectiveness was adversely affected by COD (chemical oxygen demand), as treatment effectiveness was insignificant at chlorine dioxide doses less than 8 mg/L. Chlorine dioxide dose less than 20 mg/L was ineffective for 16 of the 39 pharmaceutical ingredients (Hey et al. 2012). Overcoming the adverse effects of elevated COD or suspended solids in the effluent will obviously increase capital and operating expenses of oxidation with chlorine dioxide.

Ozonation, an advanced oxidation process (AOP), was used in a pilot-scale reactor to assess removal effectiveness of PPCPs from wastewater effluent following conventional activated sludge treatment. Oxidation rates of PPCPs, such as macrolide and sulfonamide antibiotics, estrogens, dicyfenac, naproxen and indomethacin, exceeded 90 percent with ozone doses greater than 2 mg/L (Huber et al. 2005). Unlike chlorine dioxide, ozone treatment did not appear to be adversely affected by suspended solids. Sorbed pharmaceuticals were removed equally well in both low and elevated TSS (total suspended solids) effluent streams.

**Potential in Constructed Wetland Treatment**

As even advanced technologies are highly dependent upon the physical and chemical characteristics of the CECs, it is likely that treatment of CECs will need a suite of complementary technologies, including constructed wetlands, to address the broad spectrum of CECs, PPCPs and their metabolites. As noted, removal of CECs from wastewater effluent may be accomplished by taking advantage of a combination of sorption processes and biological decompositional (a.k.a. oxidation). Given the potential to remove CECs, and the comparatively low construction and operation costs, constructed wetlands continue to get attention as a potential polishing step for wastewater treatment plant effluent.

Constructed treatment wetlands use multiple processes, such as biogeochemical reactions, photolysis and sorption, to remove contaminants through both destructive and nondestructive pathways (Hijosa-Valsero et al. 2011; Kadlec and Wallace 2009; Matamoros et al. 2009). In some cases, constructed wetlands are better at removing PPCPs from wastewater than conventional activated sludge processes, possibly due to the combination of sorption potential, plant uptake and longer retention times in wetlands (Hijosa-Valsero et al. 2011; Matamoros et al. 2009).

The treatment of pharmaceuticals in constructed wetlands depends on numerous factors, including the wetland flow regime, oxygen availability, vegetation and soil dynamics, and chemical structure of the contaminant (Verlicchi and Zambello 2014). Hydraulic retention time (HRT) and hydraulic loading rate (HLR) are commonly cited as design variables that are strongly and positively correlated with treatment of certain CECs (Durão et al. 2010; Verlicchi et al. 2012; Zhang 2012).

The tendency of CECs to sorb preferentially to soil or in the plant substrate in wetlands is indicated by the value of distribution coefficients, such as the octanol-water partition coefficient (Kow) and the solute distribution coefficient (Kd). Greater values of the Kow are associated with hydrophobic compounds, those compounds that preferentially partition into the octanol rather than into the water in a two-phase system; thus, one would expect to find CECs with low Kow in solution. Contaminant sorption in soil is largely driven by the presence and amount of soil organic matter (SOM). Therefore, wetlands provide substantial opportunity using soil, plant roots and plant detritus to treat CECs with elevated Kd.

The review by Li et al. (2014) reports that pharmaceuticals with a Log Kow between 0.5 and 3.5 are sufficiently lipophilic to move through plant cell membranes and also sufficiently water soluble to be transported into the plant cell fluids. Carbamazepine (Log Kow = 2.45) is apparently readily absorbed by Typha spp. plant roots and transported through the plant to accumulate in the leaves. Antibiotics such as ciprofloxin with Log Kow <0.5, are highly water soluble, so uptake by plants is driven by the transpiration process. Besides absorption and translocation within the plant body, plants in constructed wetlands promote the development and maintenance of microbial populations that can degrade CECs. Plant roots release oxygen into the soil, thereby driving chemical oxidation of CECs.

The Sharif (2014) study examined the effect of hydraulic loading rate (HLR) and carbon loading rate (CLR) in experimental microcosms of four CECs (two steroid hormones, atrazine and carbamazepine) where the Log Kow of the compounds ranged from 2.45 to 4.02. Increasing the HLR from 3.4 to 5.6 cm/d decreased the mass removal of each of the four compounds. Atrazine and carbamazepine removal was less than 20 percent under both HLR scenarios, while testosterone and 17-estradiol (E2) ranged from approximately 50 to 70 percent. Sorption was the primary removal mechanism for carbamazepine, whereas photolysis was responsible for removing approximately 82 percent of the atrazine.
Biodegradation of E2 and testosterone removed approximately half of the mass, while sorption and photolysis removed the remainder. In Li et al. (2014), prior research for removal efficiency of 36 pharmaceuticals in different types of constructed wetlands was summarized. Constructed wetland types included surface free water (SWF), horizontal subsurface flow (HSSF), vertical subsurface flow (VSSF) and hybrid constructed wetlands. It reported that 13 pharmaceuticals were removed in constructed wetland treatment at better than 70 percent efficiency, including acetaminophen, salicylic acid, sulfadiazine, sulfadimethoxine, sulfamethazine, sulfamethoxazole, sulpyravidine, trimethoprim, atenolol, metoprolol, furamidine, caffeine and tetracycline. In contrast, wetland treatment of ampicillin, erythromycin and lincomycin was efficient by less than 20 percent. There is limited data available regarding what type of wetland provides better performance compared to the others.

Ibuprofen, a.k.a. iso-butyl-propanoic-phenolic acid (C13H18O2), is a nonsteroidal anti-inflammatory drug (NSAID) with analgesic properties. While over 90 percent of ingested ibuprofen is excreted in the urine as metabolites, its widespread and frequent use results in measurable concentrations of ibuprofen in wastewater effluent, streams and rivers. Naproxen (C13H14O3) is the active ingredient in drugs such as Aleve®. Naproxen is also a widely used non-prescription NSAID with analgesic properties and characteristics similar to ibuprofen. Approximately 50 percent of the pharmaceutical is excreted in the urine as metabolites, whereas the majority is excreted unchanged (Deer and Leog 2013). The Log Kow (3.97 and 3.18 for ibuprofen and naproxen, respectively) indicates that both compounds have a medium sorption potential and would be good candidates for wetland treatment.

In the paper by Dordio et al. (2010), it was determined that the primary removal mechanisms of ibuprofen was adsorption to light expanded clay aggregate (LECA) and biodegradation in wetland microcosms planted with Typha spp. Removal effectiveness ranged from 82 to 96 percent under summer temperature conditions with hydraulic retention time of seven days. Removal effectiveness was significantly affected by water temperature, indicating that microbial degradation is an important process in removing ibuprofen. Over 50 percent of the influent ibuprofen was removed within the first six hours of treatment in the wetland, largely through sorption.

It is evident from the ongoing research that the presence of CECs in wastewater will continue to present challenges to the wastewater industry. Highly reactive or readily sorbed compounds appear to be the most readily treatable, yet small concentrations of higher toxicity compounds may present the greatest environmental or chronic health risk. While wetland treatment offers some opportunity as a low-cost polishing process, the effect of PPCP accumulation on the wetland biota and the risks associated with PPCP metabolites that result from biological activity have not been fully explored.

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References