Science of the Total Environment 639 (2018) 640–647

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Removal of acidic pharmaceuticals by small-scale constructed wetlands using different design configurations

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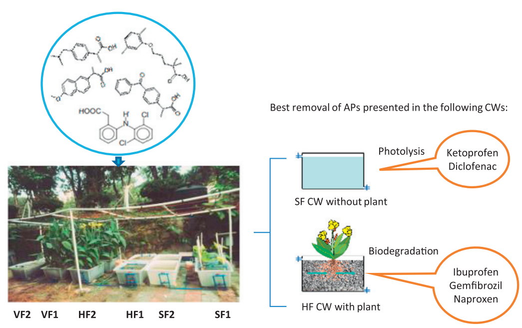
HIGHLIGHTS

- HF CWs showed high removal for ibuprofen, gemfibrozil, and naproxen.
- SF CWs performed well for the degradation of ketoprofen and diclofenac.
- Macrophytes favored the ibuprofen and gemfibrozil removal in SSF CWs.
- Water temperature and Dow of APs affect the removal of APs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 March 2018
Received in revised form 12 May 2018
Accepted 16 May 2018
Available online xxxx

Editor: D. Barcelo

Keywords:
Constructed wetland
Degradation
Emerging organic matters
Photolysis
Removal efficiency

ABSTRACT

To better understand the performance of constructed wetlands (CWs) to remove acidic pharmaceuticals (APs) in wastewaters in subtropical areas and to optimize CW design criteria, six small-scale CWs under different design configurations were operated. The factors (environmental parameters, water quality, and seasonality) influencing the APs removal were also analyzed to illustrate the removal mechanisms. The results indicated that the best performances of CWs were up to 80–90%. Subsurface flow (SSF) CWs showed high removal efficiency for ibuprofen, gemfibrozil and naproxen, but surface flow (SF) CWs performed better for ketoprofen and diclofenac. The positive relationship between the removal efficiencies of ibuprofen, gemfibrozil, and naproxen with dissolved oxygen and ammonia nitrogen reveals that SSF CWs under aerobic conditions benefit the biodegradation, while the favorable conditions created by SF CWs for receiving solar radiation promote the effective photolysis of ketoprofen and diclofenac. Planted SSF CWs had significantly higher removal efficiencies of ibuprofen and gemfibrozil than the unplanted controls had in all seasons. The removal of all APs was higher in summer and autumn than those in winter. Furthermore, an inverse relationship between removal efficiency and the distribution coefficient (logDow) was observed in SF CWs. Overall, CWs that provide aerobic degradation and photolysis would benefit APs removal in subtropical areas in the south of China.

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https://doi.org/10.1016/j.scitotenv.2018.05.198

1. Introduction

Acidic pharmaceuticals (APs) are compounds with the same carboxyl group and similar values of p*Ka* (between 3.6 and 4.9) and include analgesic anti-inflammatory drugs and lipid regulators (Lindqvist et al., 2005). Ibuprofen (IBP), gemfibrozil (GFB), naproxen (NPX), ketoprofen (KTP) and diclofenac (DCF) are types of APs that are widely detected in sewage wastewater treatment plants and the aquatic environment in concentrations ranging from $ng \cdot L^{-1}$ to $\mu g \cdot L^{-1}$ (Comeau et al., 2008; Zhao et al., 2009). Accumulated APs in aquatic ecosystems can pose threats to the environment, aquatic organisms, and human beings because of their potential toxicity (Cleuvers, 2004; Du et al., 2016; Fent et al., 2006).

Owing to advantages of low-cost, eco-friendliness, and easy operation and maintenance, constructed wetlands (CWs) have been receiving great attention since they were proved to be an efficiently way for the removal of pharmaceuticals and personal care products (PPCPs) from wastewater (Dordio et al., 2010; Hijosa-Valsero et al., 2010; Verlicchi et al., 2013; Yan et al., 2016; L Zhang et al., 2017).

Studies of APs in CWs merely focus on their removal efficiency, as reviewed by Zhang et al. (2014). Although the removal efficiency of some APs is satisfying, the removal mechanism involved is not well known. The processes affecting APs removal in CWs have not yet been thoroughly identified owing to their environmental complexity. These implied that the effects of different factors on the removal of APs and mechanisms, as well as how to improve the removal efficiency in CWs, are still not clear.

According to the literature, removal of APs involved of processes such as biodegradation, photo degradation, adsorption, depending on the design of CWs (Li et al., 2014; Verlicchi and Zambello, 2014). However, few studies have been conducted to optimize the design parameters of CWs used for APs removal. Hijosa-Valsero et al. (2010) compared the removal capacity of CWs with different flow type, vegetation, and seasonal characteristics, but their study didn't include the analysis of degradation processes of similar APs. More, the removal of APs with p*Ka* values around 3.6–4.9, especially for the widely used lipid regulator gemfibrozil, in subtropical areas such as Guangdong province of China by CWs were not that many and the seasonality effect was rarely announced.

It is therefore essential to carry out studies focusing on the removal of APs by CWs with different design configurations to examine the factors affecting their removal and the mechanisms involved, as well as to improve the removal efficiency in CWs. Previous studies reported that the ability of CWs to remove APs varied significantly, depending on the kind of APs (Li et al., 2014; Zhang et al., 2014), so it is necessary to optimize the design parameters of CWs to obtain high and stable treatment efficiency for each AP.

In this study, five APs including analgesic/anti-inflammatory drugs (ibuprofen, naproxen, ketoprofen and diclofenac) and lipid regulator (gemfibrozil) were selected because of their widespread use and hence continuous release into the environment. Among them, ibuprofen, naproxen and diclofenac are kinds of low to high aerobic biodegradable compounds (Kahl et al., 2017), while ketoprofen is readily photodegradable compounds (Matamoros et al., 2009). The physic-chemical properties of the selected APs are shown in Supplementary Table S1.

Six small-scale constructed wetlands with different flow types, presence or absence of plants were built in the present study to (i) investigate the removal efficiencies and kinetics of selected APs in CWs with various design configurations; (ii) analyze factors affecting the removal of APs, including environmental parameters, water quality, and APs' physical-chemical properties as well as design parameters; (iii) evaluate degradation mechanisms of APs, and optimize the design parameters for APs removal. The results of this study are the first step in screening for single CW with potential to remove APs to compose hybrid CWs that designed for the categories of APs removal from wastewater. To our knowledge, this is the first study reporting the removal behavior of a category of APs with similar chemical structures in CWs based on a large variety of CW design configurations in different seasons in subtropical areas.

2. Materials and methods

2.1. Experimental design

2.1.1. Description of the small-scale CWs

The experiments were carried out in 2015–2016 at Jinan University in Guangdong Province (113°17′E, 23°8′N) in summer, autumn, and winter. The average temperature in summer, autumn and winter were around 29.8, 24.8 and 15.2 °C, respectively. The annual mean sunshine duration was around 1622 h during the study period.

Since the main purpose of this study was to evaluate the removal of APs in CWs with various designs, namely free surface-flow (SF) CWs, subsurface flow (SSF) CWs including horizontal subsurface flow (HF) CWs and vertical subsurface flow (VF) CWs were operated, the absence or presence of plant were considered (Fig. 1). All these six CWs were consisted of polyvinyl chloride containers with dimension of 0.7 m × 0.5 m × 0.4 m. Washed gravel to a depth of 30 cm was used as main substrate while zeolite was used to enhance the removal of nitrogen. 5 individuals of *Canna indica* L. with a uniform size were planted as the main vegetation after root pruning and placed in the Hoagland nutrient solution for acclimation. CWs were operated under two different hydraulic retention time (HRT) for SF (2.55 d) and SSF CWs (1.27 d). More details are provided in Table S2.

2.1.2. System operation conditions

The experiments were run continuously during the whole experiment period. Each CW system was fed with synthetic wastewater instead of real wastewater for the advantage of reducing interferences during chemical analysis. The synthetic wastewater was composed of 30.8 $mg \cdot L^{-1}$ total nitrogen (TN), 15.4 $mg \cdot L^{-1}$ ammonia-N (NH_4^+-N), 2.5 $mg \cdot L^{-1}$ total phosphorus (TP) and 163 $mg \cdot L^{-1}$ chemical oxygen demand (COD) according to Wießner et al. (2005).

Standard APs working solutions were injected into synthetic wastewater to obtain a final concentration of 100 $\mu g \cdot L^{-1}$, which simulated a relatively high levels of APs found in influent of wastewater treatment plants. The synthetic wastewater was then discharged into each CW via pipes. The flowmeters were used to accurately controlling the continuous flow rate at 2 $L \cdot h^{-1}$ in all CWs.

2.2. Sampling regime

After one year's operation for stabilization, three sampling periods were set in summer (August 2015), autumn (November 2015) and winter (January 2016), separately. Twenty-four-hour composite water samples were collected from the inlet and outlet of the CWs every day for 6 days continuously in each sampling period (no rain occurred during sampling), and each sample was measured with three repetitions. The samples were collected in a 500-mL amber glass bottle, and 0.5 g NaN_3 was added to restrain the activity of microorganisms. The refrigerated samples (4 °C) were transported to the laboratory and analyzed within 24 h. Water temperature (T), dissolved oxygen (DO) and pH value were measured using a YSI meter (YSI ProPlus, Yellow Spring, Ohio 45,387 USA) and recorded onsite at the sampling time.

2.3. Analytical methodology of water quality parameters

Water samples were analyzed for general water quality parameters, including total nitrogen (TN), ammonia nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N) and chemical oxygen demand (COD) according to the standard water and wastewater monitoring and analysis method (The State Environmental Protection Administration of China, 2002). The