Environmental Pollution 184 (2014) 620–639

Contents lists available at ScienceDirect

Environmental Pollution

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

Review

Removal of pharmaceuticals and personal care products in aquatic plant-based systems: A review

Dongqing Zhang [a,*], Richard M. Gersberg [b], Wun Jern Ng [c,e], Soon Keat Tan [d,e]

[a] *Advanced Environmental Biotechnology Centre, Nanyang Environment & Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, #06-10, Singapore 637141, Singapore*
[b] *Graduate School of Public Health, San Diego State University, Hardy Tower 119, 5500 Campanile, San Diego, CA 92182-4162, USA*
[c] *Nanyang Environment & Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore*
[d] *Maritime Research Centre, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*
[e] *School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*

ARTICLE INFO

Article history:
Received 21 April 2013
Received in revised form
25 July 2013
Accepted 8 September 2013

Keywords:
PPCPs
Pharmaceuticals
Removal
Constructed wetlands

ABSTRACT

Pharmaceuticals and personal care products (PPCPs) in the aquatic environment are regarded as emerging contaminants and have attracted increasing concern. The use of aquatic plant-based systems such as constructed wetlands (CWs) for treatment of conventional pollutants has been well documented. However, available research studies on aquatic plant-based systems for PPCP removal are still limited. The removal of PPCPs in CWs often involves a diverse and complex set of physical, chemical and biological processes, which can be affected by the design and operational parameters selected for treatment. This review summarizes the PPCP removal performance in different aquatic plant-based systems. We also review the recent progress made towards a better understanding of the various mechanisms and pathways of PPCP attenuation during such phytoremediation. Additionally, the effect of key CW design characteristics and their interaction with the physico-chemical parameters that may influence the removal of PPCPs in functioning aquatic plant-based systems is discussed.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) have attracted increasing concern during the last decade because of their widespread uses and continuous release to the aquatic environment (Ternes, 1998; Ellis, 2006; Kasprzyk-Hordern et al., 2009). Due to high polarity and low volatility, most pharmaceuticals tend to be easily transported and discharged into water compartment (Breton and Boxall, 2003). Consequently, surface water sampling programs in the UK, continental Europe, North America and elsewhere have all shown the presence of many different classes of pharmaceuticals, some of which are known to be environmentally persistent (Crane et al., 2006; Zuccato et al., 2004).

Unlike veterinary medicines which may be introduced to the environment through a variety of point and diffuse sources, exposure of aquatic wild life to human pharmaceuticals is mostly to occur from point source discharge, i.e., wastewater treatment plants (WWTPs), and this exposure may therefore be at continuous and trace-level concentrations ranging from ng L^{-1} to μg L^{-1} (Daughton and Ternes, 1999). Conventional WWTPs are generally not equipped to deal with pharmaceutical compounds, as they were designed with the principal aim of removing easily or moderately biodegradable compounds (Verlicchi et al., 2012). Consequently, various kinds of pharmaceutical compounds are released into surface, ground, and coastal waters (Jones et al., 2001; Batt et al., 2006; Proia et al., 2013). Technologies including ozonation (Andreozzi et al., 2005), reverse osmosis (Kimura et al., 2009) and advanced oxidation processes (Ternes et al., 2003), as well as process optimization (e.g., increasing sludge residence time) (Carballa et al., 2007) do exist to reduce the level of pharmaceuticals compounds in water. However, these processes are not widely used because of cost effectiveness (Fent et al., 2006). Consequently, there is an increasing need for alternative wastewater treatment processes for pharmaceutical removal that have high removal efficiencies at reasonable cost.

Concerns over the possible environmental risks of continuous aquatic exposure to human pharmaceuticals have therefore led to a call by many environmental agencies worldwide (Crane et al., 2006). Since trace-level concentrations of pharmaceuticals may cause subtle chronic effects on ecosystems, the totality of their ecotoxicological impacts on the aquatic environment over the long term is difficult to predict (Daughton and Ternes, 1999; Rodríguez-

---

[*] Corresponding author.
E-mail address: dqzhang@ntu.edu.sg (D. Zhang).

0269-7491/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envpol.2013.09.009

Gil et al., 2010; Sui et al., 2010). These increasing ecotoxicological impacts on organisms in the aquatic and terrestrial environment may include development of antimicrobial resistance, decrease in plankton diversity, and inhibition of growth of human embryonic cells (Fent et al., 2006; Klamerth et al., 2010; Reinhold et al., 2010). In the meantime, the adverse effect caused by chronic aquatic toxicity on *Daphnia*, algae, higher aquatic plant and bacteria has also been demonstrated (Crane et al., 2006; Halling-Sørenen, 2000). Nevertheless, ecotoxicological data are currently available for <10% of the currently prescribed pharmaceuticals and it is also disconcerting that only a few pharmaceuticals have been subjected to ecological risk assessment (Brausch et al., 2012).

With the unique advantages of low-cost, simple operation/maintenance, and environmental friendliness, aquatic plant-based systems such as constructed wetlands (CWs) have a long history for treatment of all kinds of wastewater (Gersberg et al., 1986; Kadlec and Knight, 1996). CWs have been demonstrated to be a sustainable technology and operational alternatives to conventional WWTPs for efficient elimination of various contaminants including total suspended solids (TSS), biochemical oxygen demand (BOD_5), nitrogen, phosphorus, heavy metals and microbial contaminants (Kadlec, 2003; Vymazal, 2005). In recent years, the applicability of aquatic plant-based technologies such as CWs for the elimination of PPCPs has been increasingly explored (Matamoros and Bayona, 2006; Matamoros et al., 2008a,b).

Although aquatic plant-based systems appear to have a promising future as alternative for secondary wastewater treatment systems or as treatment units for polishing secondary effluent from WWTPs, they have been often viewed as a “black box”, with only influent and effluent concentrations measured to gauge performance and without detailed studies on the actual fate of the compounds or their pathways for removal. In aquatic plant-based systems, complex physical, chemical and biological processes may occur simultaneously, including volatilization, sorption and sedimentation, phytodegradation, plant uptake and accumulation, as well as microbial degradation (Matamoros et al., 2005; Scheytt et al., 2005; Reyes-Contreras et al., 2012; Hijosa-Valsero et al., 2010a). A general pharmaceutical removal mechanism in CWs was shown in Fig. 1. In particular, the majority of studies on pharmaceutical removal in aquatic plant-based systems have been orientated towards removal efficiency or treatment performance, and detailed investigation of removal processes such as sorption, plant uptake and biological degradation are scarce (Imfeld et al., 2009). Furthermore, the rate of these processes depends on a variety of design and operational factors such as loading mode (batch or continuous operational mode), presence of vegetation, soil matrix/substrate, depth of bed, plant species, organic and hydraulic loading rate, as well as wetland configuration, and all may exert a profound influence on the micropollutants’ removal in CWs (Ávila et al., 2013; Stottmeister et al., 2003). Additionally, the physico-chemical processes contributing to pharmaceutical degradation in CWs have not been thoroughly described (Hijosa-Valsero et al., 2010b). In this regard, there is an imperative need to lighten the “black box” to be able to understand the basic elimination and transformation processes that drive the removal of PPCPs, so as to better design CWs for optimized treatment.

This review gives an overview of the present state of researches on the removal of PPCPs by means of aquatic plant-based systems such as CWs, and focuses on an assessment and evaluation of the key removal mechanisms determining the elimination of PPCPs. In the first part, the removal performance of PPCPs under different CW configurations and in different applications is reviewed. Secondly, the main physico-chemical and biological mechanisms and pathways contributing to the elimination of PPCPs are examined. Finally, the effect of design parameters and their interaction with physico-chemical parameters which may influence PPCP removal in these aquatic plant-based systems are discussed.

2. Application performance of PPCP removal in CWs

2.1. CWs as alternative for secondary wastewater treatment systems

An overview of the physico-chemical properties for the frequently investigated PPCPs in CWs was shown in Table 1. Published researches on PPCP removal in CWs applied as alternative secondary wastewater treatment systems has focused mainly on mesocosm-scale systems and rarely on pilot- or full-scale. A summary of the design parameters (e.g., configuration and operational mode) of CWs applied as alternative secondary treatment systems was shown in Table 2. The wastewater investigated in most studies was urban wastewater or synthetic urban wastewater. Table 3 summarizes the removal efficiencies of frequently investigated PPCPs in CWs applied as alternative for secondary treatment

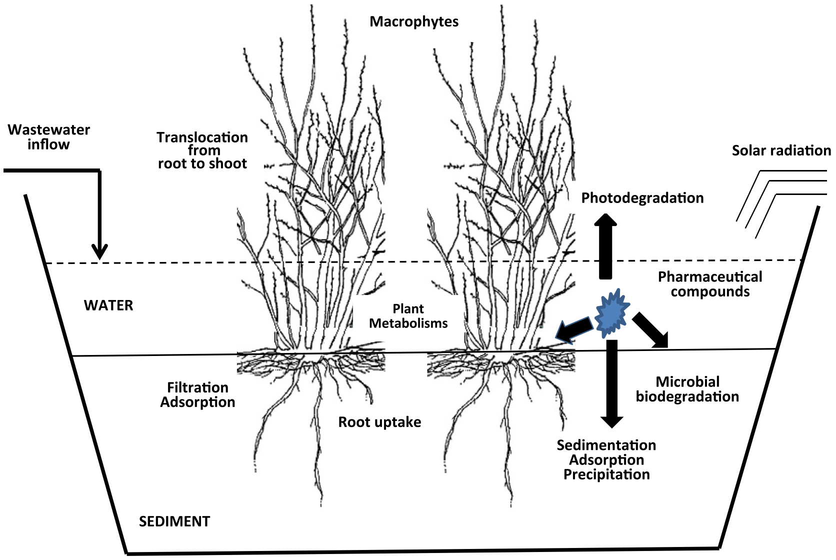

Fig. 1. Pharmaceutical removal mechanisms in constructed wetlands.