Science of the Total Environment 634 (2018) 52–58

Contents lists available at ScienceDirect

Science of the Total Environment

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

Estimating environmental fate of tricyclic antidepressants in wastewater treatment plant

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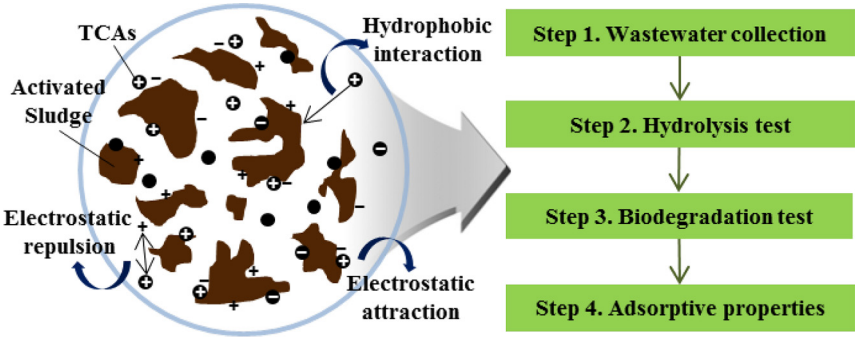
HIGHLIGHTS

- TCAs were neither readily hydrolyzed nor readily biodegraded under conditions of WWTPs.
- TCAs were quickly adsorbed onto the activated sludge via electrostatic and hydrophobic interactions.
- The adsorption affinities depended on the types of activated sludge, i.e. aerobic and anaerobic.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 January 2018
Received in revised form 19 March 2018
Accepted 23 March 2018
Available online xxxx

Keywords:
Adsorption
Hydrolysis
Biodegradation
Pharmaceutical
Tricyclic antidepressants
Activated sludge

ABSTRACT

TCAs are known to be toxicants and endocrine disrupting agents. Generally, after being used, TCAs are passed through wastewater treatment plants (WWTPs) to be treated. However, still trace amounts (ng/L to μg/L) of TCAs have been founded even in the treated water. Therefore, the aim of this study is to elucidate the environmental behaviors of TCAs in the sewage water from WWTPs (Jeonju, Korea). For the experiments, seven TCAs (amitriptyline, imipramine, clomipramine, desipramine, protriptyline, nortriptyline, and doxepin) were selected. Hydrolysibility, biodegradability, and adsorbability of the selected seven TCAs were evaluated. Based on the results, it was concluded that TCAs are not readily hydrolyzed in water and also not biodegraded by aerobic sludge. The 60% to 85% of TCAs were adsorbed immediately onto the activated sludge within 1 s via electrostatic and hydrophobic interactions. It was clearly observed that adsorption affinities were dependent on the types of activated sludge (i.e. anaerobic and aerobic sludge). The affinities of aerobic and anaerobic sludge towards the TCAs at trace concentrations e.g., 1 to 10 μg/L, were estimated to be in the range from 0.021 ± 0.000 to 0.087 ± 0.000 L/μg and from 0.001 ± 0.000 to 0.108 ± 0.001 L/μg, respectively.

1. Introduction

Numerous micropollutants such as biocides, heavy metals, antibiotic resistance genes and pharmaceuticals (Luo et al., 2014; Verliefde et al., 2007; Zhang et al., 2015) can affect the aqueous environment due to their persistent (Perazzolo et al., 2010; Sacher and Brauch, 2002) and bioactive properties (Benner et al., 2013; Cirja et al., 2008). Moreover, many of the micropollutants cannot be effectively removed by conventional sewage treatment technologies (Clara et al., 2005; Zhang et al., 2008) and the untreated chemicals may be released out to the natural environments (Altmann et al., 2014). It is believed that the continued

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https://doi.org/10.1016/j.scitotenv.2018.03.278
0048-9697/

release of micropollutants from wastewater effluents causes long-term risks, leading to bioaccumulation (Bervoets et al., 2009; Nesto et al., 2007) and formation of new mixtures in aqueous environments (Bervoets et al., 2009; Schwarzenbach et al., 2006).

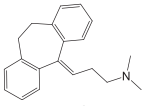
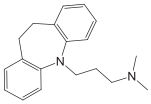
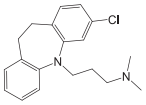
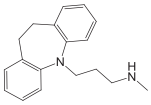
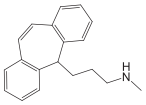
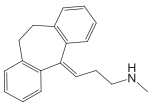
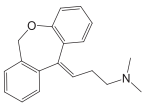
Particularly, the disposals of pharmaceuticals are becoming an environmental issue. Actually, it has been reported that pharmaceuticals are a new class of compounds known as emerging pollutants, which have attracted considerable interest in recent years (Daughton, 2004). Additionally, the untreated yet still bioactive pharmaceuticals can eventually return to humans via the food chain (Schwarzenbach et al., 2006; Verliefde et al., 2007; Zhang et al., 2008). Previous investigations have demonstrated that some pharmaceuticals can be removed during treatment processing by the adsorption and biodegradation by biological sludge (Joss et al., 2005; Joss et al., 2006; Pomiès et al., 2013; Xia et al., 2018). However, their removal efficiencies depend on the operating conditions of wastewater treatment plants (WWTPs) such as sludge retention time, hydraulic retention time, and temperature (Clara et al., 2005; Kim et al., 2005; Kreuzinger et al., 2004).

Among the pharmaceuticals, tricyclic antidepressants (TCAs) are frequently used for the treatment of mood disorders (Liu et al., 1998). Moreover, the consumption of TCAs has been increasing over the past few decades (Willner et al., 1987); the usage of TCAs increases by an average of 10% per year. This implies that TCAs are being released or found more frequently than previously because the release of TCAs is hardly controlled and is present throughout various pathways e.g. human urine (Gram and Overø, 1972; Salem et al., 2004). Indeed, TCAs have been frequently detected in aqueous environments (Borova et al., 2014; Tsai et al., 2016; Wen et al., 2008). The exposed TCAs can cause several side effects e.g., anticholinergic (Khawam et al., 2006) and cardiovascular diseases (Glassman and Bigger, 1981), sedation (U'Prichard et al., 1978), weight gain (Berken et al., 1984), and sexual side effects (Hsu and Shen, 1995). In order to avoid these side effects, it is important to understand the environmental fate of the TCAs in WWTPs where the TCAs are first treated.

Several techniques including reverse osmosis (Radjenović et al., 2008), adsorption (Urase and Kikuta, 2005), UV (Pereira et al., 2007), and ozone treatment (Vogna et al., 2004) have been investigated for the removal of micropollutants. Among these techniques, adsorption is considered one of the most simplest and efficient methods due to the vast variety of adsorbents (Bediako et al., 2017; Verlicchi et al., 2012). Most WWTPs were originally designed to control a wide range of materials such as particulates, nutrients, and carbonaceous materials. Most of these contaminants can generally be efficiently removed. Moreover, aerobic and anaerobic treatment has received great interest in the last few decades due to its several benefits (e.g. low energy consumption) (Chan et al., 2009; Christgen et al., 2015). However, the removal of micropollutants is often not effective (Luo et al., 2014). For example, although previous studies reported the treatment of some TCAs using activated sludge, the removal efficiencies were focused on, but there was lack of information about the environmental fate (Baker and Kasprzyk-Hordern, 2013; Hörsing et al., 2011; Hyland et al., 2012; Kasprzyk-Hordern et al., 2009; Verlicchi et al., 2012). It is highly likely that information regarding the stability (e.g. hydrolysis), biodegradation and adsorptive properties (e.g. affinity and equilibrium properties of TCAs with activated sludge) are fundamental and essential to understand, which would help to lay down proper protocols for their effective treatment.

This study thus focuses on the environmental fate of 7 cationic TCAs in WWTPs, which include amitriptyline (AMI), imipramine (IMI), clomipramine (CLO), desipramine (DES), protriptyline (PRO), nortriptyline (NOR), and doxepin (DOX) (Table 1). The specific aims of this research are to (i) evaluate the hydrolysibility and biodegradability of TCAs by aerobes in the aqueous environment of WWTPs, (ii) investigate the contribution of adsorption onto the surface of activated sludge in the removal of TCAs, and (iii) compare the adsorption affinities of aerobic and anaerobic sludge at trace concentrations.

Table 1
Physical properties of the tricyclic antidepressants.

TCAs	Chemical structure	Molecular weight (g/mol)	pK_a	Log K_{ow}
Amitriptyline$^+$		277.40	9.76	4.92
Imipramine$^+$		280.41	9.40	4.80
Clomipramine$^+$		314.85	9.20	5.19
Desipramine$^+$		266.38	10.02	4.90
Protriptyline$^+$		263.38	10.54	1.18
Nortriptyline$^+$		263.38	10.47	4.51
Doxepin$^+$		315.84	9.76	0.67