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Review

Analysis and advanced oxidation treatment of a persistent pharmaceutical compound in wastewater and wastewater sludge-carbamazepine

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HIGHLIGHTS

- A review on occurrence, risk analysis, quantification and degradation of CBZ
- Publicly available information is insufficient for conclusive risk analysis on humans
- Current status is discussed with extraction, detection and degradation options
- The ozone based AOPs have gained the widest application for removal of carbamazepine
- Some treatment produce by-products which are more toxic than the parent compounds

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ABSTRACT

Pharmaceutically active compounds (PhACs) are considered as emerging environmental problem due to their continuous input and persistence to the aquatic ecosystem even at low concentrations. Among them, carbamazepine (CBZ) has been detected at the highest frequency, which ends up in aquatic systems via wastewater treatment plants (WWTPs) among other sources. The identification and quantification of CBZ in wastewater (WW) and wastewater sludge (WWS) is of major interest to assess the toxicity of treated effluent discharged into the environment. Furthermore, WWS has been subjected for re-use either in agricultural application or for the production of value-added products through the route of bioconversion. However, this field application is disputable due to the presence of these organic compounds and in order to protect the ecosystem or end users, data concerning the concentration, fate, behavior as well as the perspective of simultaneous degradation of these compounds is urgently necessary. Many treatment technologies, including advanced oxidation processes (AOPs) have been developed in order to degrade CBZ in WW and WWS. AOPs are technologies based on the intermediacy of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end products. The purpose of this review is to provide information on persistent pharmaceutical compound, carbamazepine, its ecological effects and removal during various AOPs of WW and WWS. This review also reports the different analytical methods available for quantification of CBZ in different contaminated media including WW and WWS.

Contents

Abbreviations: AOP, advanced oxidation process; ASE, accelerated solvent extraction; APCI, atmospheric pressure chemical reactions; CBZ, carbamazepine; GC-MS, gas chromatography–mass spectrometry; HPLC, high performance liquid chromatography; II, irradiation intensity; LI, light intensity; LLE, liquid–liquid extraction; LOD, limit of detection; LC-MS, liquid chromatography–mass spectrometry; LC-MS/MS, liquid chromatography–mass spectrometry/mass spectrometry; LDTD, laser diode thermal desorption; MAE, microwave-assisted extraction; MEC, measured environmental concentration; PhACs, pharmaceutically active compounds; PNEC, predicted no-effect environmental concentration; SE, Soxhlet extraction; SFE, supercritical fluid extraction; SPE, solid phase extraction; UV, ultra violet; VAP, value added products; WWTP, wastewater treatment plant; WW, wastewater; WWS, wastewater sludge.

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1. Introduction

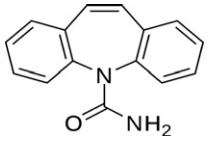
Large volumes of pharmaceuticals are used for the prevention, diagnosis and treatment of diseases in human and animals. Pharmaceutically active compounds (PhACs) have become a subject of great interest to environmental researchers worldwide (Hao et al., 2007). The worldwide average per capita consumption of pharmaceuticals per year is estimated to be about 15 g and in industrialized countries, the value is expected to be in between 50 and 150 g (Alder et al., 2006). Due to their extensive use, presence in the aquatic environment and their potential for impacts on wildlife and humans, it is becoming an important environmental issue (Fent et al., 2006). To date, most attention has been focused on identification, fate and distribution of PhACs in municipal wastewater treatment plants (WWTPs), which are commonly found at very low concentrations (ppb level or low) (Radjenovic et al., 2009; Verlicchi et al., 2012). Many chemical, physical and biological factors, such as adsorption on biosolids, pH, ionic strength of the sewage, and the physico-chemical properties of PhACs may affect the fate of PhACs in WWTPs. Among different chemical properties of PhACs that co-operate in defining its fate in WWTP, some hydrophilic compounds may remain in the dissolved form in the aqueous phase of the WWTP effluent, or hydrophobic substances may bind to the biosolids. Hence, these compounds may enter the environment through the discharge of WWTP effluents into receiving water or they may enter the environment in association with biosolids that are ultimately disposed to agricultural lands.

Carbamazepine (CBZ) was the most frequently detected pharmaceutical residue in water bodies (Zhang et al., 2008). CBZ (5H-dibenzo [b,f]azepine-5-carboxamide) is a drug sold under the commercial name Tegratol. CBZ is used alone or in combination with other medications to control certain types of seizures. It is also used to treat trigeminal neuralgia (a condition that causes facial nerve pain). CBZ extended-release capsules (Equetro brand only) are used to treat episodes of mania (frenzied, abnormally excited or irritated mood) or mixed episodes (depression that happens at the same time) in patients with bipolar I disorder (manic-depressive disorder; a disease that causes episodes of depression, episodes of mania, and other abnormal moods) (Prajapati et al., 2007). CBZ is a class of medications called anticonvulsants. It works by reducing abnormal electrical activity in the brain. CBZ is also sometimes used to treat mental illnesses, depression, posttraumatic stress disorder, drug and alcohol withdrawal, restless leg syndrome, diabetes insipidus, certain pain syndromes, and a disease in children called chorea (Miao and Metcalfe, 2003). The physico-chemical properties of CBZ are summarized in Table 1.

Following human administration, CBZ has been detected in wastewater (WW) and wastewater sludge (WWS). Studies in Europe and North America have shown that CBZ is one of the most frequently detected pharmaceuticals in WWTP effluents and in river water (Metcalfe et al., 2003a, 2003b; Gao et al., 2012; Mohapatra et al., 2012). Researchers considered that CBZ could be a "witness molecule" confirming the presence and persistence of drugs in water bodies (Clara et al., 2004). Furthermore, pre-treatment of WW and WWS is adopted to remove the organic compounds and improve the solubilization of sludge (Weemaes and Verstraete, 1998). Various methods employed for sludge pre-treatment include, mechanical treatment (Tiehm et al., 2001), chemical treatment (Bougrier et al., 2006), alkaline and thermo-alkaline treatment (Vlyssides and Karlis, 2004), oxidative treatment (Huber et al., 2003), photocatalytic treatment (Doll and Frimmel, 2004), radiation treatment (Lafitte-Trouque and Forster, 2002) and biological treatment (Chong et al., 2011). However, the choice of either one of these pre-treatment methods depends on the cost of the process and other factors, such as concentration and volume of the effluent to be treated.

As WWTPs provide the first and perhaps the most important opportunity for removing CBZ that are destined for discharge into the environment. WWTPs were constructed with the aim to remove carbonaceous compounds (organic matter) and nitrogen and P compounds arriving at concentrations of mg/L. In order to remove micropollutants, more recent and conventional treatments are not always able to guarantee this aim, but in some cases they can remove some compounds. Therefore, it is important to characterize the fate of CBZ during the treatment of municipal WW and WWS. Furthermore, in order to protect the ecosystem and end users or create public awareness on beneficial uses of WWS, it must be free from any kind of organic compounds including CBZ (subjected to future regulation for treated effluent before their discharge in aquatic environment). Hence, it is required to study the fate of CBZ during or after pre-treatment of WW and WWS and secure an innovative practice for discharge of WW to river and sludge recycling and reuse. Further, the measurement problems associated with quantification of these pharmaceutical compounds including CBZ in WW and WWS are to detect the analyte in trace levels (ng L^{-1} or below) and to avoid the impact on the analyte signals caused by matrix components. The purpose

Table 1
Physico-chemical and pharmacological properties of CBZ.

Structure	
Molecular formula, CAS no. and molecular weight	$C_{15}H_{12}N_2O$, 298-46-4 and 236.27 g mol^{-1}
Water solubility	17.7 mg L^{-1} (20 °C)
Log K_{ow} (octanol–water partitioning)	2.45
Henry's law constant	1.09×10^{-5} Pa m^3 mol^{-1} (25 °C)
p*Ka*	13.90
Melting point	189–193 °C
Usage	Analgesic, anticonvulsant, antimanic agent
Appearance	White, light yellowish powder
Toxicity	Mild ingestion causes vomiting, drowsiness, ataxia, slurred speech, nystagmus, dystonic reactions, and hallucinations. Severe intoxications may produce coma, seizures, respiratory depression and hypotension
Affected organisms	Human and aquatic organisms

References: www.chemicalbook.com, www.SigmaAldrich.com, www.alfa.com.