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The fate of typical pharmaceuticals in wastewater treatment plants of Xi'an city in China

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ABSTRACT

Eight typical pharmaceuticals in four wastewater treatment plants (WWTPs) of Xi'an city in China were investigated to determine their occurrence and removal efficiencies. Target pharmaceuticals were extracted from wastewater and sludge samples by solid-phase extraction (SPE) and analyzed by gas chromatography equipped with tandem mass spectrometry (GC–MS/MS) after derivatization. The results indicated that the concentrations of the pharmaceuticals ranged from 0.39 to 642 $\mu g\,L^{-1}$ in the influents, which were similar with or one order magnitude higher than that of previous reports, and phenacetin, gemfibrozil and caffeine were main contributors. The concentrations in the effluents were between 0.075 and 7.01 $\mu g\,L^{-1}$, and 80–100% pharmaceuticals were removed in the WWTPs except diclofenac, which was removed nearly 72–85%. Three main removal pathways including physicochemical process, biodegradation and sludge adsorption were involved in the removal of the pharmaceuticals. Almost 20–50% of the pharmaceuticals were removed through physicochemical operating units, and high concentration pharmaceuticals were examined in the floating oil from aerated grit chamber. Nearly 11–89% and 0–15% pharmaceuticals were removed by biodegradation and sludge adsorption, respectively. Aerobic condition was advantageous for the biodegradation of phenacetin, gemfibrozil and caffeine, while cholesterol was easily decomposed by anaerobic microorganism. It showed that high temperature was beneficial to the biological removal of gemfibrozil, and acidic condition could be more helpful to the biodegradation of diclofenac and its removal efficiency reached 60% at pH 4.5. However, biodegradability of diclofenac should be further investigated to eliminate its adverse effects on human health and ecological environment.

Introduction

As the stricter wastewater discharge standards and increasing requirement of water recycle, pharmaceuticals in the aquatic environment have received much more attentions due to their adverse effects on human health and ecological environment [1]. Nowadays, pharmaceuticals have been detected in wastewater, surface water, underground water and even drinking water at the level of $ng\,L^{-1}$ to $\mu g\,L^{-1}$ [2–4], which would cause direct toxicity to certain aquatic organisms [5] or result in irreversible change on wildlife [6,7] and human beings by slow accumulation [8]. Pharmaceuticals mainly come from excrement of sick humans and animals, discharged wastewater and solid waste of hospitals and pharmacy companies etc. Wastewater treatment plants (WWTPs), as the sink and source of municipal wastewater, are much easier to be monitored and controlled compared with fugitive discharge spots. The quality of treated effluent can have direct positive impact on receiving river and other aquatic environments. Therefore, the occurrence and removal of trace pharmaceuticals in wastewater of the WWTPs should be a priority. A number of studies had been carried out in North America [9], Europe [10], Japan [11] and Republic of Korea [12] etc. The reported results revealed that pharmaceuticals existed in the wastewater with variable concentrations and had different removal efficiencies in primary, secondary and tertiary treatment due to different usage patterns, compound-specific properties, types of biological treatment processes and variable technical parameters such as hydraulic retention time (HRT), sludge age (SA) and wastewater temperature etc. In China, similar studies had been reported in recent decades which mainly focused on concentration determination, analytical method, and advanced oxidation treatment processes [13–16], but these researches were still at their infancy. As well known, the WWTP is primarily designed to remove suspended solids and grit, dissolved nutrient and organic compounds, ammonia nitrogen and phosphorus etc., but not especially considered for the elimination of aquatic pharmaceuticals.

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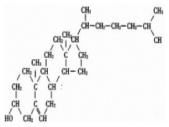
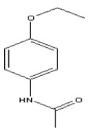
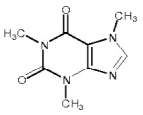
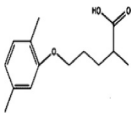
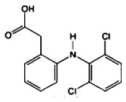
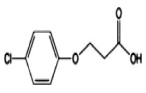
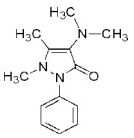
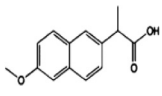
Therefore, it is critical to investigate the occurrence and removal efficiencies of the pharmaceuticals in the WWTPs. Key influencing factors, such as hydraulic retention time (HRT), water temperature, pH and initial concentration, should be investigated and analyzed, which could be helpful to improve the removal of pharmaceuticals in wastewater. However, relatively few studies have been conducted in north-western area of China.

In this study, the occurrence and removal of eight pharmaceuticals were ascertained in four WWTPs with different biological treatment processes in Xi'an city, China. For eight pharmaceuticals, diclofenac (DCF), phenacetin (PNT), pyramidon (PMD) and naproxen (NPX) are analgesics, gemfibrozil (GFZ) and clofibric acid (CA) are antilipidemic drugs, caffeine (CAF) is a stimulant and cholesterol (CH) is a lipidic compound. Key influencing factors of biodegradation were also optimized to understand how to better remove pharmaceuticals as well as how to improve the quality of discharged wastewater by adjusting operating parameters slightly in the WWTPs. This research will be very meaningful for removing trace pharmaceuticals more effectively.

Table 1
Molecular structures and physicochemical properties of target pharmaceuticals [16,17].

	MS	pK_a	log K_{ow}	MP (°C)	LOD (ng/L)	AR (%)	RSD (%)
Cholesterol		–	8.7	141.5	2.8	93	20.4
Phenacetin		2.1	1.6	137.5	1.0	88	11.2
Caffeine		10.4	−0.07	238	1.3	95	18.5
Gemfibrozil		4.7	4.8	167	0.9	73	9.9
Diclofenac		4.2	0.7	174.6	0.8	85	18
Clofibric acid		3.2	2.6	186	1.7	86	15.4
Pyramidon		5.0	1.0	108	0.5	73	8.9
Naproxen		4.2	3.2	155.3	0.8	88	14.9

Note: MS, molecular structure; MP, melting point; LOD, limit of detection; AR, average recovery; RSD, relative standard deviation.