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Research article

Investigation of relationships between removals of tetracycline and degradation products and physicochemical parameters in municipal wastewater treatment plant

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ABSTRACT

Determination of the effect of physicochemical parameters on the removal of tetracycline (TC) and degradation products is important because of the importance of the removal of antibiotics in Wastewater Treatment Plant (WWTP). Therefore, the purpose of this study was to investigate the relationships between removals of TC and degradation products and physicochemical parameters in Municipal Wastewater Treatment Plant (MWWTP). For this aim, (i) the removals of physicochemical parameters in a MWWTP located in Elazığ city (Turkey) were determined (ii) the removals of TC and degradation products in MWWTP were determined (iii) the relationships between removals of TC and degradation products and physicochemical parameters were investigated. TC, 4-epitetracycline (ETC), 4-epianhydrotetracycline (EATC), anhydrotetracycline (ATC), and physicochemical parameters (pH, temperature, electrical conductivity (EC), suspended solids (SS), BOD_5, COD, total organic carbon (TOC), NH_4^+–N, NO_2^-–N, NO_3^-–N and O–PO_4^{-3}) were determined. The calculation of the correlation coefficients of relationships between the physicochemical parameters and TC, EATC, ATC showed that, among the investigated parameters, EATC and SS most correlated. The removals of other physicochemical parameters were not correlated with TC, EATC and ATC.

1. Introduction

Approximately 3000 different pharmaceuticals ingredients are used in the European Union, including antibiotics, beta-blockers, lipid regulators, antidepressants and many more, for human consumptions (therapeutic or diagnostic purposes) (Ternes and Joss, 2006; Al Aukidy et al., 2012). The antibiotics taken by living beings are disposed from living metabolism as unchanged or little transformed (Topal et al., 2012).

Wastewater Treatment Plants (WWTPs) effluents represent a significant source of the pharmaceuticals in the environment, as their elimination rates are often insufficient (Pailler et al., 2009; Škrášková et al., 2013). Although antibiotics are commonly detected in aquatic environments only at sub-inhibitory concentration levels (from ng/L to μg/L), their long-term presence tends to cause a genetic selection of resistant bacteria (Baquero et al., 2008; Bao et al., 2013).

Since the 1950s, tetracycline (TC) antibiotics have been widely used in human and veterinary medicine to treat bacterial infections and promote animal growth (Hopkins and Blaney, 2014). TCs are poorly absorbed by the digestive system with mostly excreted unmetabolized, and a portion of them still remains biologically active in waste (Halling-Sorensen et al., 2002; Dai et al., 2012). Active part of TC in urine is approximately 20–55% (Dökmeci, 1985). Human excretion rate for TC in the aquatic environment is high (≥70%) (Luo et al., 2014). TCs have been detected in wastewaters from WWTPs with concentrations of 10–1000 ng/L (Miao et al., 2004; Lindberg et al., 2005; Batt et al., 2006, 2007; Karthikeyan and Meyer, 2006; Thomas et al., 2007; Gulkowska et al., 2008; Li and Zhang, 2011; Gao et al., 2012; Leung et al., 2012).

Because of the being one of the most popular classes of antibiotics, having produced global sales of $1.6 billion in 2009 (Hamad, 2010) and also elimination in faeces and urine (Brinzila et al., 2012), TCs were selected for the study. Elazığ Municipal Wastewater

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Treatment Plant (EMWWTP) was selected for investigation in the present study because (i) in the other study of us (Topal et al., 2013) the occurrence of TC was proved in that treatment plant and (ii) the treatment plant takes all of the wastewaters (domestic, industrial, commercial, hospital etc.) of the city.

The knowledge about the occurrence and removal of the antibiotics in the WWTPs is important because of the negative effects (long time presence, antibiotic resistance, toxicity, stress on ecosystem e.g.) of them in the receiving environments. Therefore, determination of the antibiotics and the degradation products in the WWTPs which are the main sources of antibiotics in the receiving environments is important. Also, investigation of the relationships between removals of TC and degradation products (4-epianhydrotetracycline, anhydrotetracycline) and physicochemical parameters is important to understand if the removals of TC and degradation products are negatively or positively related to physicochemical parameters or not. Therefore, in the present study, correlation analysis was used to identify the physicochemical parameter affecting the removals of TC, 4-epianydrotetracycline (EATC) and anhydrotetracycline (ATC). In the literature, to our knowledge, there is not any study about the investigation of the relationships between removals of EATC, ATC and physicochemical parameters in WWTPs. Also, there are only limited studies concerning the relationships between removals of antibiotics and physicochemical parameters in WWTPs. Karthikeyan and Meyer (2006) reported a weak relationship between TC reduction and the suspended solid (SS) removal. He et al. (2015) reported relationships for removals of fluoroquinolone antibiotics and background wastewater quality parameters. Watkinson et al. (2007) reported that total antibiotic concentration correlate with nitrate in the conventional treatment plant. Sari et al. (2014) observed higher correlation between diclofenac and SS concentrations among conventional parameters in the influent.

2. Materials and methods

2.1. Chemicals and reagents

In this study, Tetracycline (TC, 98%) (Sigma–Aldrich, USA), 4-epitetracycline (ETC, 97%) (Acros Organics, USA), anhydrotetracycline (ATC, 97%) (Acros Organics, USA) and 4-epianhydrotetracycline (EATC, 97%) (Acros Organics, USA) were analyzed. Oasis HLB (500 mg, 6 cm^3) (Waters Corporation, Milford, MA, USA) and Oasis MAX (60 mg, 3 cm^3) (Waters Corporation, Milford, MA, USA) were used as solid-phase extraction cartridges.

2.2. Description of the wastewater treatment plant

The municipal wastewater treatment plant (MWWTP) in Elazığ, Turkey was chosen in this study. Elazığ MWWTP (EMWWTP) is located in Mollakendi-Yünlüce, Elazığ-Bingöl road at 17th km. The location of EMWWTP is given in Fig. 1 (This figure is revised from Topal and Arslan Topal (2015)). EMWWTP serves a population of 383.975 equivalent inhabitants.

Necessary calculations were done according to the years 2000 and 2020 with taking future population of Elazığ city and equivalent population of various industries when EMWWTP was projected. It was estimated that the population of Elazığ city in year 2020 will be 512.956 person and the used water amount for per person will be 250 L/person day. It was accepted in the project that 70% of the used water will be given to the sewage. The treatment plant was projected as 2 levels: Project flow as 820 L/s for year 2000 and 1671 L/s for year 2020. The wastewater treatment process in plant consists of pre-treatment (screens), a grit chamber and cyclic activated sludge system, followed by a secondary clarifier. Also there is a UV disinfection unit for the disinfection of the secondary effluent before discharge. But this unit is not under operation. In year 2007, the revision was made in EMWWTP that was taken into operation in year 1994. The revisions were addition of the mechanic bar screen to the system and renovation of the reinforced concrete part, renovation of the grit chamber, construction of aeration grit chamber, centrifuged pump usage instead of screw pump, renovation of the reinforced concrete part of clarifiers and aeration tanks, change of the draw palettes of the secondary clarifiers, change of the pallette system of the thickening tank, addition of UV disinfection system and setup of the Belt Press system instead of sludge drying beds. After these changes EMWWTP again taken to the operation in year 2008 (Topal and Arslan Topal, 2011; Topal et al., 2014).

The general component of influent of the wastewaters of EMWWTP is given in Table 1.

2.3. Sample collection

Composite samples of 24 h from influent and effluent of the EMWWTP were taken. Coordinates of UTM WGS84 6° which belong to the sampling points are given in Table 2. Wastewater samples for analyses of TC and degradation products were collected in 0.5 L bottles (prewashed with 0.25 g/L Na_2EDTA water solution, methanol, and ultrapure water and dried before use). Wastewater samples for analyses of physicochemical parameters were collected in 0.5 L bottles. pH, temperature, electrical conductivity (EC) values were measured at the plant. After the protection conditions taken at +4° C, samples were transferred to the laboratory of the Fırat University Environmental Engineering Department and immediately analyzed (Topal et al., 2014).

2.4. Physicochemical parameters

pH, temperature, EC values and SS, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total organic carbon (TOC), (amonnium nitrogen) $NH_4^+{-}N$, nitrite nitrogen ($NO_2^-{-}N$), nitrate nitrogen ($NO_3^-{-}N$) and orthophosphote ($O{-}PO_4^{-3}$) concentrations were determined in influent and effluent of wastewater samples. pH and temperature values were measured by pH Orion SA 720 while EC values were measured by EC Delta OHM. SS values were determined according to the Standard Methods (AWWA et al., 1989; Topal et al., 2014). COD, $NH_4^+{-}N$, $NO_2^-{-}N$, $NO_3^-{-}N$ and $O{-}PO_4^{-3}$ concentrations were analyzed by Nova 60 Spectroquant. TOC and BOD_5 concentrations were analyzed by Hach Lange DR3800 spectrophotometer.

2.5. Sample extraction and UFLC-MS/MS instrumental analysis for TC and degradation products

Analyses were performed by Solid Phase Extraction (SPE) and ultra fast liquid chromatography-tandem mass spectrometry (UFLC-MS/MS) using the method reported by Jia et al. (2009). The samples collected were filtered with a glass microfiber filter (0.7 μm, Whatman, Maidstone, England). After filtration, 150 mL influent and 300 mL effluent were added with 0.5 g/L Na_2EDTA, and acidified to pH 3.0 with hydrochloric acid. Oasis HLB cartridges were preconditioned with methylene chloride, methanol and ultrapure water containing 0.5 g/L Na_2EDTA (adjusted to pH 3.0 with HCl). The samples were passed through the cartridges. Oasis HLB cartridges were rinsed with ultrapure water, dried under a flow of nitrogen and then eluted with methanol. The eluates were dried under a flow of nitrogen and reconstituted to 0.3 mL with methanol. The extracts were diluted to 8 mL by ultrapure water (pH 7.0 with 5% $NH_3{\cdot}H_2O$). The solutions were applied to the Oasis MAX