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Letrozole and tamoxifen in municipal wastewater and their photodegradation in ultraviolet (UV) treatment

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Abstract The incidence of cancer has increased worldwide and hormone antagonists are a group of pharmaceuticals used in the treatment of breast cancer. It is well known, that most of the pharmaceuticals are only partially removed or transformed during traditional wastewater treatment processes and the residues enter the environment through wastewater effluents. In aquatic environment, these pharmaceuticals pose a risk, as they may cause adverse effects on development and reproduction of organisms. In this study, the presence of two hormone antagonists, letrozole and tamoxifen, in wastewater influent and effluent samples was determined. Ultraviolet (UV) treatment is widely used technique to disinfect wastewater and drinking water. The potential of UV irradiation to degrade these selected pharmaceuticals was also studied in laboratory conditions. Preliminary results show the presence of studied pharmaceuticals in wastewater samples at low ng/L levels. Tamoxifen showed high degradation rates in UV treatment, whereas letrozole seemed to be quite resistant. Further studies to determine the occurrence of studied pharmaceuticals in environment are in progress. The experiments to improve the UV treatment are also planned.

Keywords: hormone antagonists, wastewater, photodegradation, emerging contaminants

1. Introduction

Over the last years, the concern of the presence of pharmaceutical residues in the environment has increased. Wastewater treatment plants (WWTPs) are the main sources of pharmaceutical residues, as the existing treatment processes are not designed to remove this kind of contaminants and these processes are not efficient enough. At the same time, the incidence of cancer has increased worldwide and cancer is one of the leading causes of human deaths worldwide. There are many studies of the fate and occurrence of various kind of pharmaceuticals in wastewaters and surface waters (Fent et al. 2006, Ternes 1998), but anticancer drugs are often overlooked in environmental studies (Jureczko & Kalka 2020, Kosjek & Heath 2011,). Letrozole and tamoxifen belong to the group of hormone antagonists, which are often used to treat breast cancer. These pharmaceuticals effect on the function and synthesis of hormones and due to their mode of action, they may cause adverse effects on development and reproduction of aquatic organisms (Liao et al. 2015, Sun et al. 2007a, Sun et al. 2007b).

As pharmaceutical residues enter the water bodies in wastewater effluents, there is a need to develop more effective treatment technologies. Ultraviolet (UV) irradiation is widely used to disinfect drinking water and wastewater treatment plants use it as a tertiary treatment to improve the microbiological quality of the effluent (Hijnen et al. 2006, Kovacic et al. 2016). Previous studies have shown that it is also a potential way to degrade pharmaceuticals (Pereira et al. 2007). Different kind of advanced oxidation processes (AOPs) and another advanced treatment processes like membrane filtration have also been used to remove and degrade pharmaceuticals from wastewaters (Zhang et al. 2013), but as the local wastewater treatment plant uses UV technique as a tertiary treatment, we decided focus on that.

The aims of this study were to validate analytical methods to detect letrozole and tamoxifen in wastewater samples collected from local wastewater treatment plants and determine the concentrations in wastewater samples. Finally, we wanted to determine the effectiveness of ultraviolet (UV) irradiation to degrade these pharmaceuticals in laboratory scale experiments.

2. Materials and methods

2.1. Sample collection and pretreatment

The presence of selected pharmaceuticals in wastewater was studied from influent and effluent samples collected from two local wastewater treatment plants located in Lahti (Finland). Samples (24 h-composite samples) were collected during four separate sampling periods between April 2019 and January 2020. Samples were transferred to laboratory, filtered with glass fiber filter (GF/A, 1.6 µm Whatman) and stored at -20 °C until analysis. The extraction of letrozole and tamoxifen from wastewater samples (sample volume 200 mL) was done by using Oasis HLB (500 mg, Waters) solid-phase extraction

(SPE) cartridges, which were selected by preliminary tests. For validation of the method, analytes were spiked into ultrapure water and wastewater samples in two concentrations and the relative and absolute recoveries were calculated. The analysis of letrozole and tamoxifen was carried out by using liquid chromatography system coupled to a triple quadrupole mass spectrometer (LC-MS/MS) with electrospray ionization (Waters Corp., Milford, MA, USA).

2.2. Laboratory scale UV experiments

To study the photodegradation of selected pharmaceuticals, the UV experiments were carried out in laboratory conditions. Experiments were performed by using a small UV device (volume 300 mL) containing low-pressure mercury lamp (LP/UV, power 6 W) emitting UV C radiation at wavelength of 254 nm. Analytes were spiked (200 ng per sample) into wastewater and ultrapure water samples (sample volume 300 mL), which were treated with UV C for predetermined times. Treatment times were between zero to 360 seconds (ultrapure water) and zero to 690 seconds (wastewater).

3. Results

The preliminary results show that letrozole and tamoxifen can be found from wastewater influents at low ng/L concentrations. Letrozole was also found from effluent samples. The UV experiments showed high degradation rates for tamoxifen, as its concentration decreased up to 96 % in wastewater samples and even more in ultrapure water. On the other hand, letrozole seemed to be quite resistant towards UV C radiation. Further studies to determine the occurrence of selected compounds in the environment are currently in progress. The experiments to improve the UV treatment are also planned to take place in near future.

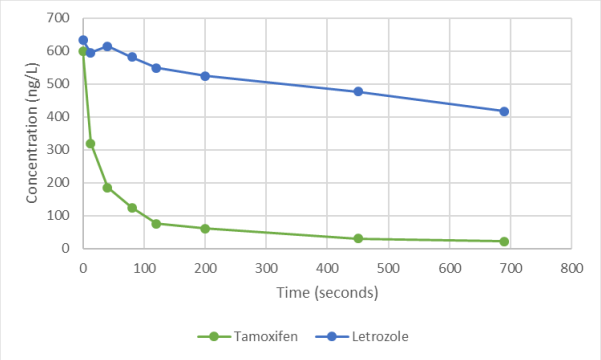

Figure 1. Degradation of letrozole and tamoxifen in spiked wastewater samples in UV experiments.

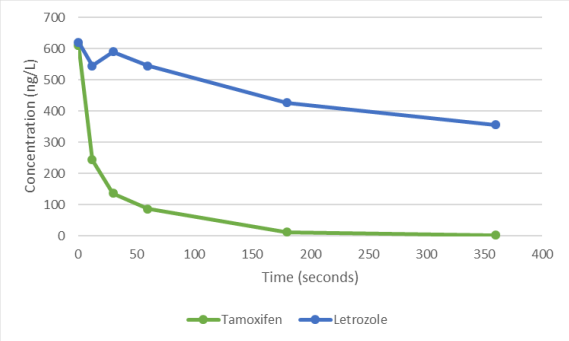

Figure 2. Degradation of letrozole and tamoxifen in spiked pure water samples in UV experiments.

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