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EFFICIENCIES OF CONVENTIONAL ANAEROBIC DIGESTION PROCEDURE AND IONIZING RADIATION TREATMENT FOR REMOVAL OF PHARMACEUTICAL RESIDUES FROM MUNICIPAL WASTEWATER

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Nowadays, pharmaceutical products (PPs) have raised global concerns due to accumulation of their residues in aquatic ecosystems. In the urban environment, epidemics and social factor illnesses, advancement of pharmaceutical industry, hospitals and other health-care institutions, veterinary institutions pharmaceutical industries and uses in household need are the main economic sources or factors influencing emerging dissemination of PPs in the environment [1].

Presence of several PPs in the environment is recognised to represent a danger for living species in aquatic ecosystems and several human health issues such as allergic, hypertonic, toxicological influences, hormonal disturbance, and bacterial tolerance to antibacterial medicines in case of antibiotics [2-3]. That determines high importance of management strategies needed to determine contaminating PPs and their levels and to improve recycling strategies of wastewaters entering the municipal wastewater treatment plants (WWTPs) in order to prevent the release of PPs in surface water aquifers.

The treatment procedures of wastewaters arriving at conventional municipal WWTPs used in most of countries including Latvia are based on activated sludge process (aeration basins) or anaerobic digestion (biological treatment) basins, which have noted to be effective to recycle water by reducing levels of contaminants up to > 80% [4]. However, the studies of effluents discharged from the WWTPs after the treatment stages by sludge or biological treatment procedures have shown limited capabilities on the degradation of several pharmaceuticals such as antibiotics, antidepressants, steroidal drugs and other PPs [5]. Recently, the applications and research of advanced oxidation treatment procedures by chemical (ozone, chlorination), nonionizing (UV radiation) or ionising radiation (sources of X-rays, gamma rays, accelerated electrons, etc.) on the degradation of pharmaceuticals in aquatic solutions and in WWTP applications have notably expanded due to promising advantages of PP decomposition extents especially for hardly decomposable PPs (macrolides, quinolones, sulphonamides, etc. antibiotics, hormones, etc. PPs) [4, 6].

In the frame of the noted issues, the present study was performed in order to compare the decomposition of eighteen multi-class pharmaceuticals (analgesics, nonsteroidal anti-inflammatory drugs (NSAIDs), cytostatic anticancer drugs, antibiotics) prior to their treatment and after the treatment by two procedures – full recycling cycle of the WWTP (effluent samples were tested) or the exposure of influent samples to ionizing radiation generated by accelerated electron flux from linear particle accelerator of 5 MeV energy.

For the sample collecting and their treatment, the Riga city central WWTP "Daugavgriva" was used, which is the largest facility in Latvia dedicated to recycling of municipal WWs and serving a population of ca. 698,529.

The WW samples were collected over 24-h period from the influent basin and the recycled samples collected from the effluent collector (five replicates of each sample were applied). All the samples were sampled in pre-cleaned 1 L amber glass bottles and kept at +4ºC during the transportation. Once arrived in the laboratory, the samples were immediately

filtered through 1.2 µm glass microfiber filters (GF/C, Whatman, UK) and extracted within 24 h using Strata X solid phase extraction cartridges.

Besides the conventional treatment of wastewater influents under the Daugavgriva WWTP, exposure to ionising radiation by a 5-MeV electron beam (EB) radiation was tested on the collected influent samples. Prior to irradiation, samples were packaged in bags, which had the thickness of 2-3 mm held during the irradiation. The linear particle accelerator ELU-4 (Elektronika, former Soviet Union) was used for the irradiation of samples. The samples were irradiated at ambient temperature up to 5 and 15 kGy absorbed EB radiation doses at the dose rate of 1,200 kGy/h. The irradiation of the samples was performed from both sides.

In general, the techniques of analytical assessment should be of high sensitivity and reliability not only to be as a tool of target analysis on basis of the match of determined PPs with the standards, but to screen the levels of potential compounds and their metabolites in aquatic systems at more expanded level of investigation. However, the high resolution mass spectrometric (HRMS) detection based chromatographic methods may have a prominent role on target assessment of multi-class PP emerging mycotoxins in WW samples before and after the treatment under different conditions thus allowing control of the treatment efficiency in the WWTP facility. In last decade, high resolution mass spectrometric detection techniques based on the Orbitrap- HRMS technology and the recent of time of flight HRMS detectors have released in the market with high benefits of their resolution and detection sensitivity especially applicable for the screening of emerging contaminants such as PPs in several environmental samples [7].

In the present research, our previously developed technique of high-performance liquid chromatography coupled to Orbitrap high-resolution mass spectrometry (HPLC-Q-Orbitrap-HRMS) was used to determine and quantitate PPs in the samples prior to both treatment conditions (influent samples) and after the procession in the WWTP (effluents) or exposure to EB radiation (the irradiated influent samples), respectively.

The obtained results for PP concentration levels prior and after the recycling of WW in WWTP are shown in Figure 1.

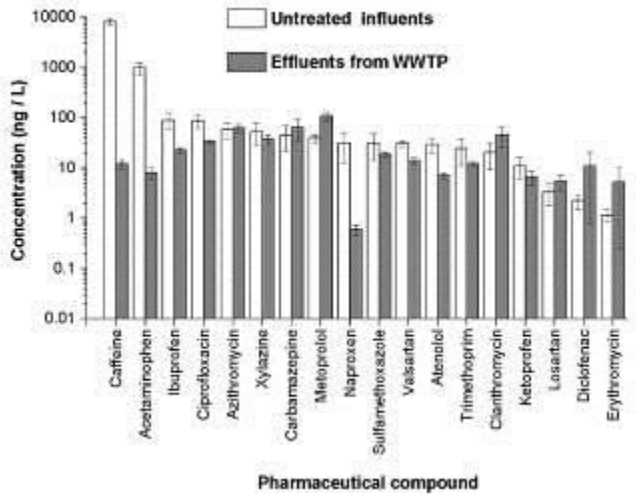

Figure 1. PP in the analysed WW prior (influents) and after (effluents) treatment in the WWTP.

The studies have revealed caffeine and acetaminophen (e.g., paracetamol) ranging between the levels of and 7.0-11.4 µg/L and 0.56-1.0 µg/L as the predominant compounds among eighteen PPs determined in the influents. In general, the levels of most compounds were in the range from 1.2 to 90 ng/L. Among another compounds widely expressed in the effluents, ibuprofen was found alt levels up to 89.5 ng/L indicating it as the most disseminated NSAID among four determined compounds (diclofenac, ibuprofen, ketoprofen),

and naproxen) The results of the study also indicated a wide concentration range (1.1-87.1 ng/L) of six multi-class antibiotics (ciprofloxacin, three macrolides – azithromycin, clarithromycin, erythromycin, and two antibacterial drugs commonly used as a mixture – trimethoprim and sulfamethoxazole).

The results of PP concentrations determined in the samples collected directly after the final effluents indicated sufficient degradation (> 50%) only for four, mainly small molecular PPs (caffeine – 99%, acetaminophen – 97%, naproxen – 90%, ibuprofen – 55%). Atenolol and trimethoprim showed insufficiently low but positive degradation ranging between 11-25%. The presented study indicated that 79% of PPs had insufficient degradation during the treatment, thus raising issues of the impact on the contamination of surface waters. The study results presented in Figure 1 indicate wide variety of pharmaceutical residues determined in the discharged effluents, where sometimes the levels even exceeded the concentrations quantified prior to the treatment as found especially in case of macrolide antibiotics. The reasons for the determined low degradation efficiency of antibiotics in the WW treated in the WWTP may be attributed to the dissolution of PPs from solid wastes such as faeces, bile, and other biogenic matter into forms free WW and the enzymatic reactions affecting poisoning of biological reagents in anaerobic basin thus infecting their ability to treat PPs (Fig. 1) [5].

The studies of the EB treatment (Figure 2) indicated that most of the PPs found at low initial levels (<50 ng L-1) were decomposed effectively at 5 kGy radiation dose (decomposition rate was >95%).

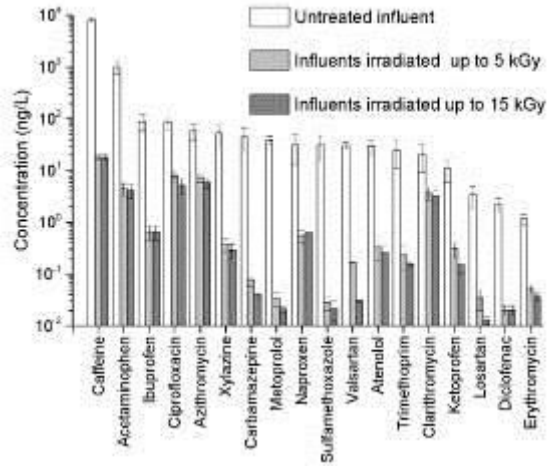

Figure 2. PPs in the analysed WW prior (influents) and after EB treatment up to 5 and 15 kGy.

However, the sample analysis after 5 kGy irradiation revealed the presence of relatively high residual concentrations of caffeine, acetaminophen, NSAIDs and selected antibiotics (macrolides and one fluoroquinolone – ciprofloxacin), the levels of those compounds decreased with the dose. Our study revealed that three analysed macrolides remained at high levels after the irradiation with up to 5 kGy absorbed doses, as already noted in the discussion above, and had the lowest degradation rates at 5 kGy. The degradation rate of those compounds was above 90% with the raise of absorbed dose up to 15 kGy, respectively.

The results of the study reveal of notable advance of highly sensitive HPLC-Q-Orbitrap-HRMS analytical method, which can be efficiently applied to determine the presence of eighteen emerging pharmaceuticals in waste water samples at nanogram sensitivity, thus ensuring excellent reliability of the method for the studies of wastewater contamination with pharmaceutical residues and establishing the degradation efficiency of ionising radiation treatments. It could be concluded that electron beam radiation may be sufficiently used to decompose pharmaceuticals in wastewater and the technique show potential uses to be applied as combination to WWTP based on biological treatment and enabling sufficient

decomposition of multi-class pharmaceuticals as noted in this study. It should be noted that linear particle accelerators emitting electrons may be more feasible in future compared to gamma sources based on radioactive isotopes due to the radiation safety and life-cycle management and the material consumption compared to conventional treatment technologies.

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