How effective is the removal of the micropollutants at the wastewater treatment plants?

Lucia Ivanová

Abstract

Aim of this study was to determine the removal efficiency of the selected pharmaceuticals at one of the WWTPs in Bratislava. Half of the studied compounds was removed from wastewater with the removal efficiency higher than 75%. Most of the pharmaceuticals were removed from the wastewater by the biodegradation. However, fexofenadine, verapamil, sertraline, citalopram, amitriptyline and alfuzosin were removed by sorption. Results of environmental risk assessment showed that antibiotics are potential risk for environment.

Keywords: biodegradation, sorption, wastewater treatment plant

1 Introduction

Interest in pharmaceuticals, personal care products and endocrine disruptors has increased over the last decade because of their potential bioactive impact on the environment (Kümmerer, 2009). These compounds are continually discharged into the environment and their usual concentrations are low. However, they can affect water quality and have a potential unfavorable impact on the drinking water, ecosystems and human health (Yuan *et al.*, 2013). The presence of these compounds in the environment has been recently quantified and has been recognized as a potentially danger for the ecosystem (Rivera-Utrilla *et al.*, 2013). This fact has forced the European Union in its Commission Implementing Decision 2015/495 of 20 March 2015 to create watch list that includes the first pharmaceutical active substances (diclofenac, 17α-ethinylestradiol, 17β-estradiol, estrone, erythromycin, clarithromycin and azithromycin). Purpose of this list is to collect monitoring data and confirm the risk properties of these substances.

The drugs are discharged into the environment in many ways. The main sources of pharmaceuticals in the environment are effluents from wastewater treatment plant (WWTP) and leakages from the landfill. The micropollutants are not completely removed during the wastewater treatment processes and therefore are often detected in surface waters in the concentration range from several ng/L to several μg/L in the extreme cases. Contamination of the environment by the micropollutants can also occur by the applying stabilized sludge (biosolids) to agricultural soil because of the possible desorption of the micropollutants from the sludge. Sources of veterinary medicaments in the soil also can be excrements of animals (Ebele, Abou-Elwafa Abdallah and Harrad, 2017).

A wastewater treatment plant consisting of a primary treatment based on physicochemical removal of the compounds and secondary treatment with a activated sludge system has a limited efficiency for a removal of micropollutants from wastewater (Rivera-Utrilla *et al.*, 2013). The main possible ways of the removal of micropollutants in activated sludge systems include biodegradation, sludge sorption, stripping and evaporation from the surface of the reactor. However, stripping and evaporation from surface of the reactor are negligible for most of the micropollutants, since the Henry's law constant would have to be higher than 100 $Pa.m^3/mol$ (Byrns, 2001). It is important to notice that common Henry's law constant for pharmaceuticals are in the range from 10^{-7} to 10^{-18} $Pa.m^3/mol$ (Zhang *et al.*, 2014).

Biodegradation is the biological process where complicated molecules of the micropollutants are converted to compounds with lower molecular weight or completely converted to CO_2 and H_2O

(Pomiès *et al.*, 2013). Degradation of the micropollutants highly depends on the structure of target micropollutants (Besha *et al.*, 2017). In general, the easily degraded substances include hydrocarbons with short side chains, unsaturated aliphatic compounds, and compounds possessing electron donating functional groups. On the other hand, the persistent micropollutants contain compounds with long, highly branched side chains, saturated or polycyclic compounds, and compounds possessing sulfate, halogen or electron withdrawing functional groups. However, for some pharmaceuticals there is not relationship between the chemical structure and their biological removal (Luo *et al.*, 2014). Molecular weight and structure of compounds are also related. It was found out that with increasing molecular weight of the compound is increasing possibility of the biodegradation of this compound, which is caused by more accessible spots for initiation of the degradation by microorganisms (Tadkaew *et al.*, 2011). In general, compounds with a molecular weight more than 300 g/mol are easier to biodegrade (Besha *et al.*, 2017).

The hydrophobicity of the compounds plays an important role in the removal of micropollutants by sorption. The hydrophobicity of the substances is characterized by the distribution coefficient K_{ow} (Cirja *et al.*, 2008). Coefficient K_{ow} is defined as the ratio of the equilibrium distribution of the compound in octanol (non-polar solvent) and in water (polar solvent). If the compounds dissociate at different pH as at pH = 7, a D_{ow} coefficient is used (Besha *et al.*, 2017). Relation between coefficient K_{ow} and D_{ow} are following:

1. for acidic compounds:

$$\log D_{ow} = \log K_{ow} - \log(1 + 10^{(pH - pK_a)})$$

2. for basic compounds:

$$\log D_{ow} = \log K_{ow} - \log(1 + 10^{(pK_a - pH)})$$

With increasing of the hydrophobicity of compound (increasing log K_{ow} or log D_{ow}) is increasing sorption of this compound into activated sludge (Cirja *et al.*, 2008; Besha *et al.*, 2017). Removal of the very hydrophobic (Log D_{ow} > 3.2) compounds is probably dominated by sorption to the activated sludge facilitating enhanced biological degradation in some cases. As the Log D_{ow} value of the compounds decreased to below 3.2, sorption of these organic contaminants onto the activated sludge is not a dominating removal mechanism (Tadkaew *et al.*, 2011).

In general, primary treatment - sedimentation tanks (removal by sorption onto primary sludge) do not represent significant removal of pharmaceuticals. Ortiz de García et al. (2013) found out that 83 % of investigated pharmaceuticals in their research have been removed up to 20 % by primary treatment. However, removal efficiencies in the range from 50 to 75 % in the sedimentation tank was found of for ciprofloxacine, clarithromycine, sulfapyridine, oxazepam and THC-COOH (Bodík *et al.*, 2016) and removal efficiencies up to 60 % were found out for atorvastatin, bezifibrate, desogestrel, fluvastatin, irbesertan, simvastatin, and tamoxifen (Ortiz de García *et al.*, 2013).

More studies published that 75 % of pharmaceuticals is removed on the conventional WWTPs (D'Alessio *et al.*, 2018; Paíga *et al.*, 2019), however different compounds have showed different efficiencies of their removal. Removal efficiency up to 80 % was published for antibiotics. Especially ß-lactam and quinolone antibiotics are easy to remove on the WWTP (Watkinson, Murby and Costanzo, 2007). Removal efficiency more than 90 % was found out for acetaminophen (Brown and Wong, 2018; D'Alessio *et al.*, 2018), but also for caffeine, cotinine, gemfibrozil, ibuprofen, methamphetamine, morphine and naproxen (D'Alessio *et al.*, 2018). High removal efficiency (up to 80 %) was published for natural and synthetic estrogens (Liu and Wong, 2013). Removal efficiencies in the wide range was published for trimethoprim (from 0 to 100 %), carbamazepine (from 0 to 98 %), sulfamethoxazole (from 0 to 75 %) and sulfadiazine (from 33 to 96 %) (D'Alessio *et al.*, 2018). However, there have been found out compounds which are hard to remove on the conventional WWTP, like for example propranol or thyroxine (Brown and Wong, 2018).

Aim of this study is to determine the removal efficiency of the selected pharmaceuticals at one of the WWTPs in Bratislava and identify if removal of compounds is caused by sorption or by biodegradation. End of the study is dedicated to the environmental risk assessment of the selected compounds.

2 Material and Methods

Sampling and analysis

To define removal efficiency of the selected WWTP, 24-h composite samples of influent and effluent from investigated WWTP were collected 2 times for analysis. Samples were collected by using an automatic sampler device in 15-min intervals across 24 h and samples were collected in plastic bottles and frozen (−20 °C) during the 2 h after sampling. Samples of the sludge were taken after the stabilization and after the dewatering. Containers prepared for transport from WWTP were sampled and a sample of sludge (approximately 500 mL) was taken 3 times for analysis. Each sludge sample was homogenized and frozen (-20 ºC) until analyse.

Pharmaceuticals from collected sludge samples were extracted by a 2-step extraction procedure described in Golovko et al. (2016). Briefly, 2 g of sludge was extracted with 4 mL of acetonitrile/water (1/1 v/v with 0.1% formic acid), ultrasonicated for 15 min, and the supernatant was filtered through a syringe filter (0.45 µm, regenerated cellulose) into 10 -mL vials. In the second step, the same procedure was repeated with 4 mL of acetonitrile/2-propanol/water (3/3/4 v/v/v with 0.1% formic acid). The sludge extracts were mixed and stored in a freezer at -20 °C until the LC-MS/MS analysis.

Isotope-labeled internal standards were added to 10 ml of homogenized and filtered (0.45 µm, regenerated cellulose) sample of the influent, effluent and sludge extract prior to the analysis.

All LC-MS/MS analyses were performed on a TSQ Quantiva triple-stage quadrupole mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) coupled to an Accela 1250 LC pump (Thermo Fisher Scientific) and an HTS XT-CTC autosampler (CTC Analytics AG, Zwingen, Switzerland). A Hypersil gold aQ column (50 mm × 2.1 mm ID × 5 µm particles; Thermo Fisher Scientific) was used for the chromatographic separation. A detailed description of MS/MS transitions and LC-MS/MS methods has been provided elsewhere (Lindberg *et al.*, 2014; Golovko *et al.*, 2016).

Calculation of the removal efficiency of pharmaceuticals

The removal efficiency (*RE*) of the pharmaceuticals was determined from concentrations of the pharmaceuticals in influent and effluent by the following equation:

$$RE = \frac{\rho_{Ii} - \rho_{Ei}}{\rho_{Ii}} \cdot 100 \qquad [\%]$$

Where:

ρ_{Ii} is concentration of compound *i* in the influent (ng/L) and ρ_{Ei} is concentration of compound *i* in the effluent (ng/L).

The mass fractions of pharmaceuticals in the sludge were analysed in 3 independent sludge samples (because of the long sludge retention time on the wastewater treatment plant and the mixing sludge in the stabilization process is really hard to decide when sludge represents inflow for selected day) and average of these values was used for calculations of the removal efficiency of the compounds by sorption (RE_{sorp}) and it was determined by the following equation:

$$RE_{sorp} = \frac{w_i \cdot \dot{m}}{\rho_{Ii} \cdot \dot{V}} \cdot 100 \qquad [\%]$$

Where:

w_i is average mass fraction of the compound i in the sludge (ng/g); $\dot{m}$ is amount of the dewatered sludge per day (g/d); ρ_{Ii} is concentration of compound *i* in the influent (ng/L) and $\dot{V}$ is inflow on the WWTP (L/d).

The removal efficiency of the pharmaceuticals by the biodegradation (RE_{bio}) was determined by the following equation:

$$RE_{bio} = RE - RE_{sorp} \qquad [\%]$$

Calculation of risk quotient

The risk quotient (*RQ*) was calculated as a ratio of measured average concentrations of pharmaceuticals in effluent and the predicted no-effect concentration (PNEC) based on the chronical or acute date depending on available values from the literature (Minguez *et al.*, 2016; WET Center, 2016) by the following equation:

$$RQ_i = \frac{\rho_{Ei}}{PNEC_i}$$

Where:
ρ_{Ei} is concentration of compound *i* in the effluent (ng/L) and $PNEC_i$ is predicted no-effect concentration of compound *i* in fresh water.
It is important to notice that the environmental risk assessment calculation is based on the downstream concentration of the compounds, however in this study will be used the concentration of the compounds in the effluent which represents the worst-case scenario.

3 Results and discussion

Removal efficiency of the pharmaceuticals at the WWTP

In this study was analyzed 93 compounds from the group of pharmaceuticals and drugs and in this study are presented pharmaceuticals, which concentrations in the influent were detected above the detection limits. They were divided in 6 groups for the practical reasons, namely analgesics and antiflogistics, antibiotics, antihistamines, compounds with effect on cardiovascular system, compounds with effect on central nervous system and group of others, where are all compounds which does not belong to groups mentioned above. The removal efficiency of the pharmaceuticals at one of the WWTPs in Bratislava was calculated as it was described in previous part of this study. All results of RE, RE_{sorp} and RE_{bio} are summarized in the table 1.
Morphine, diclofenac and tramadol belonging in the group of analgesics and antiflogistics were removed at the WWTP mostly by the biodegradation. Morphine and diclofenac had RE higher than 90 %, however tramadol had RE only 35 %. High removal of morphine was also mentioned in the literature (D'Alessio *et al.*, 2018).
RE for the group of antibiotics was in the wide range (from 25 to 93 %). Published removal efficiency 80 % (Watkinson, Murby and Costanzo, 2007) was not reached for most of the studied antibiotics. However, there was detected same trend for the removal of macrolides and sulfonamides. Both groups are mainly removed by biodegradation and slight sorption mechanism of removal was detected only for azithromycin and sulfamethoxazole. In general, higher RE was detected for the group of macrolides (from 64 to 93 %) and RE for sulfonamides was below 36 %.
Fexofenadine, cetirizine and diphenhydramine was detected in the influent and the effluent. Their removal efficiency was in the range from 47 to 89 %. It was found out that the main mechanism of the removal for fexofenadine is sorption and specifically 71 % was removed by the sorption. However, this determination is contrary with published log K_{ow} = 0,3 (CENTER FOR DRUG EVALUATION AND RESEARCH, 2010), which should mean that the sorption is not dominating removal mechanism (Tadkaew *et al.*, 2011) Sorption is also one of the mechanisms of the elimination for cetirizine and diphenhydramine, but in the slight amount.
The biggest studied group was group of the compounds with effect on cardiovascular system. Majority of the compounds from this group (8 from 12) had RE higher than 90 %. RE for other compounds from this group was in the range from 52 to 75%. Sorption was the dominating mechanism of the removal for verapamil. This determination is also proved by published log K_{ow} in the range from 3,79 to 4,8 (Verlicchi and Zambello, 2015). Sorption was also one the mechanisms of removal for atorvastatin, bezafibrate and fenofibrate, however in the slight amount. Main removal mechanism for most of the compounds from this group (8 from 12) was the biodegradation.

Table 1: The removal efficiency, the removal efficiency by the sorption and the removal efficiency by the biodegradation on the WWTP in Bratislava (grey highlighting is used for the compounds which main mechanism of the removal is sorption)

Compound	**Therapeutic group**	**RE [%]**	**RE_{sorp} [%]**	**RE_{bio} [%]**
Morphine	analgesics + antiflogistics	95	4	91
Diclofenac	analgesics + antiflogistics	92	11	81
Tramadol	analgesics + antiflogistics	35	3	32
Clarithromycin	antibiotics	93	0	93
Erythromycin	antibiotics	87	0	87
Azithromycin	antibiotics	64	3	61
Trimethoprim	antibiotics	57	0	57
Sulfapyridine	antibiotics	36	0	36
Sulfamethoxazole	antibiotics	25	2	23
Fexofenadine	antihistamines	89	71	18
Cetirizine	antihistamines	87	12	75
Diphenhydramine	antihistamines	47	17	30
Valsartan	cardiovascular system	100	1	99
Rosuvastatin	cardiovascular system	100	1	99
Atorvastatin	cardiovascular system	99	13	86
Fenofibrate	cardiovascular system	99	45	54
Telmisartan	cardiovascular system	96	1	95
Bezafibrate	cardiovascular system	93	11	82
Verapamil	cardiovascular system	93	93	0
Atenolol	cardiovascular system	90	0	90
Irbesartan	cardiovascular system	75	2	73
Diltiazem	cardiovascular system	74	5	69
Metoprolol	cardiovascular system	69	5	64
Bisoprolol	cardiovascular system	52	3	49
Caffeine	central nervous system	100	0	100
Sertraline	central nervous system	88	88	0
Donepezil	central nervous system	59	24	35
Mirtazapine	central nervous system	59	16	43
Citalopram	central nervous system	55	55	0
Amitriptyline	central nervous system	47	47	0
Oxazepam	central nervous system	44	3	41
Venlafaxine	central nervous system	39	18	21
Carbamazepine	central nervous system	33	9	24
Glimepiride	others	98	25	73
Codeine	others	69	1	68
Alfuzosin	others	60	35	25

Another studied group was group of the compounds with effect on central nervous system. Only two compounds from this group had the removal efficiency higher than 80 %, namely caffeine with RE = 100 % and sertraline with RE = 88 %. However, main mechanism of the removal for these compounds is different. In the case of caffeine, main mechanism is the biodegradation and in the case of sertraline, main mechanism is the sorption. This determination is also proved by published log K_{ow} (0,16 for caffeine and 5,29 for sertraline) for these compounds (Verlicchi and Zambello, 2015). Obtained RE for caffeine is also similar with published removal efficiency (more than 90 %) for this compound (D'Alessio *et al.*, 2018). RE for other compounds from this group was in the range from 33 to 59 %. Sorption of these compounds is one of the mechanisms of removal for almost all detected

compounds. Sorption is the slight mechanism of removal (below 10 %) only for carbamazepine and oxazepam.
Last investigated compounds were glimepiride with RE = 98 %, codeine with RE = 69 % and alfuzosin with RE = 60 %. Biodegradation was the only mechanism of the removal for codeine and main mechanism of the removal for glimepiride. Sorption was main mechanism of the removal for alfuzosin, which is contrary to published log K_{ow} = 1,51 (WET Center, 2016).
Clarithromycin, sulfapyridine, oxazepam, atorvastatin, bezafibrate and irbesartan were in the literature described like compounds which are removed in the primary treatment and it was expected that sorption of these compounds on the primary sludge is main removal mechanism (Ortiz de García *et al.*, 2013; Bodík *et al.*, 2016). However, our study did not prove this expectation. Based on our results, clarithromycin, sulfapyridine, oxazepam, atorvastatin, bezafibrate and irbesartan are first sorbed on the primary sludge, but afterwards they are removed by the biodegradation in anaerobic digestion.

Environmental risk assessment

To understand the potential risk associated with the pharmaceuticals in the effluent from the WWTP, hazard assessment using the risk quotient was conducted. The worst-case scenario was used in this study, so it means that concentrations of the compounds in the effluent were used for the environmental risk assessment. Compounds are categorized based on the RQ values as following: RQ ≤ 0,1 low environmental risk compounds; 0,1 < RQ < 1 medium environmental risk compounds and RQ ≥ 1 high environmental risk compounds. Pharmaceuticals, for which were PNEC values available in the literature are presented in the figure 1.

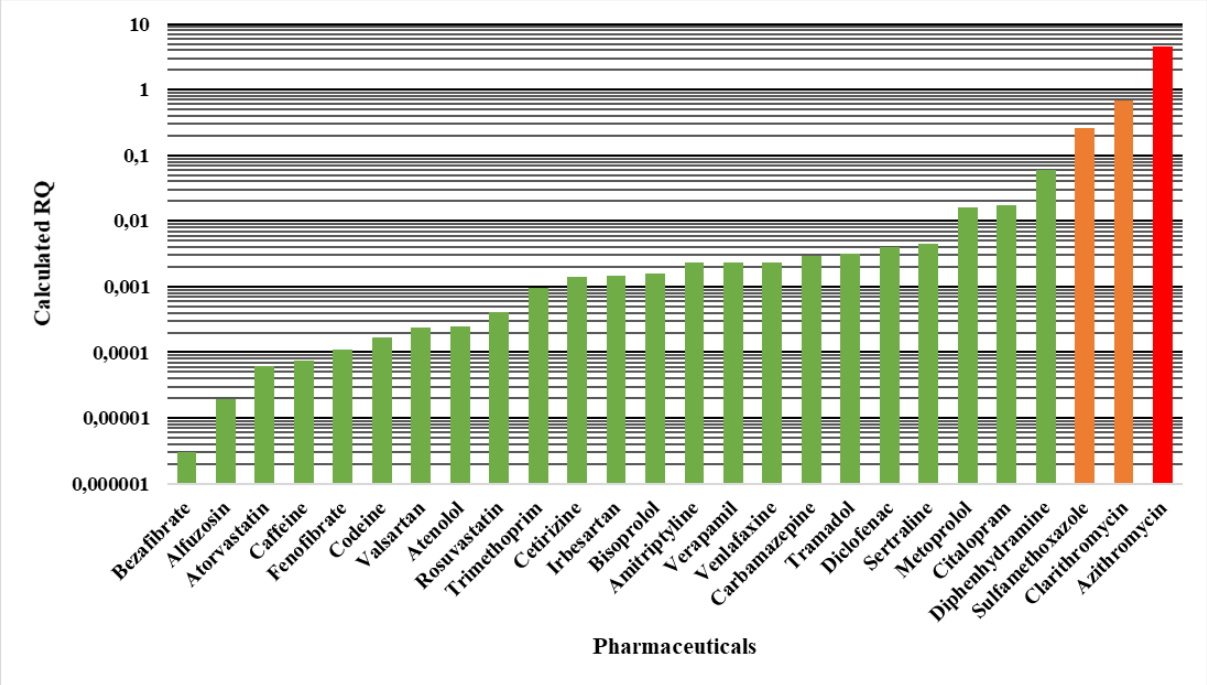

Figure 1: Risk quotients for selected pharmaceuticals (green – RQ ≤ 0,1 low risk; orange – 0,1 < RQ < 1 medium risk; red – RQ ≥ 1 high risk)

Most of the compounds investigated in this study (23 from 26) represents low risk for the environment, even if they will occur in similar concentrations in the rivers. Concentrations of the pharmaceuticals in the river water were published in one order lower than in the effluent (Luo *et al.*, 2014). However, RQ for sulfamethoxazole and clarithromycin were in the range from 0,1 to 1. It means that these compounds represent medium risk for the environment. Really high RQ was calculated for azithromycin (RQ = 4,5), which means that this compound represents high risk for the

environment. Based on our results, antibiotics represents potential risk for environment and it is appropriate that EU decided to monitor their concentrations in the fresh water.

4 Conclusion

Removal efficiency for 36 pharmaceuticals occurring in the wastewater was detected in this study. Half of the studied compounds was removed from wastewater with the removal efficiency higher than 75%. Most of the pharmaceuticals were removed from the wastewater by the biodegradation in activated sludge system or in the anaerobic stabilization of the sludge. Sorption represented main mechanism for 6 compounds, namely fexofenadine, verapamil, sertraline, citalopram, amitriptyline and alfuzosin, which may be problem in the case of using sludge for agricultural purposes. It is necessary to search for methods which will be able to remove antibiotics from wastewater because the results of environmental risk assessment showed that the antibiotics are potential risk compounds in the environment.

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5 References

Besha, A. T. *et al.*, 2017: *Removal of emerging micropollutants by activated sludge process and membrane bioreactors and the effects of micropollutants on membrane fouling: A review*, Journal of Environmental Chemical Engineering. 5(3), pp. 2395–2414

Bodík, I. *et al.*, 2016: *Drogy a lieky v odpadových vodách Slovenska - A čo s tým?* in Odpadové vody 2016, pp. 315–320.

Brown, A. K. and Wong, C. S., 2018: *Distribution and fate of pharmaceuticals and their metabolite conjugates in a municipal wastewater treatment plant*, Water Research. 144, pp. 774–783.

Byrns, G., 2001: *The fate of xenobiotic organic compounds in wastewater treatment plants*, Water Research, 35(10), pp. 2523–2533.

CENTER FOR DRUG EVALUATION AND RESEARCH, 2010: *ENVIRONMENTAL ASSESSMENT. APPLICATION NUMBER:201373Orig1s000*. Available at: https://www.accessdata.fda.gov/drugsatfda_docs/nda/2011/201373Orig1s000EA.pdf (Accessed: 15 October 2018).

Cirja, M. *et al.*, 2008: *Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR)*, Reviews in Environmental Science and Biotechnology, 7(1), pp. 61–78.

D'Alessio, M. *et al.*, 2018: *Occurrence and removal of pharmaceutical compounds and steroids at four wastewater treatment plants in Hawai'i and their environmental fate*, Science of the Total Environment, 631–632, pp. 1360–1370.

Ebele, A. J., Abou-Elwafa Abdallah, M. and Harrad, S., 2017: *Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment*, Emerging Contaminants, 3(1), pp. 1–16.

Golovko, O. *et al.*, 2016: *Development of fast and robust multiresidual LC-MS/MS method for determination of pharmaceuticals in soils*, Environmental Science and Pollution Research, 23(14), pp.

14068–14077.

Kümmerer, K., 2009: *The presence of pharmaceuticals in the environment due to human use - present knowledge and future challenges*, Journal of Environmental Management 90(8), pp. 2354–2366.

Lindberg, R. H. *et al.*, 2014: *Occurrence and behaviour of 105 active pharmaceutical ingredients in sewage waters of a municipal sewer collection system*, Water Research, 58, pp. 221–229.

Liu, J. L. and Wong, M. H., 2013: *Pharmaceuticals and personal care products (PPCPs): A review on environmental contamination in China*, Environment International, 59, pp. 208–224.

Luo, Y. *et al.* (2014) 'A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment', *Science of the Total Environment*. Elsevier B.V., 473–474, pp. 619–641. doi: 10.1016/j.scitotenv.2013.12.065.

Minguez, L. *et al.*, 2016: *Toxicities of 48 pharmaceuticals and their freshwater and marine environmental assessment in northwestern France*, Environmental Science and Pollution Research, 23(6), pp. 4992–5001.

Ortiz de García, S. *et al.*, 2013: *Consumption and occurrence of pharmaceutical and personal care products in the aquatic environment in Spain,* Science of the Total Environment, 444, pp. 451–465.

Paíga, P. *et al.*, 2019: *Assessment of 83 pharmaceuticals in WWTP influent and effluent samples by UHPLC-MS/MS: Hourly variation,* Science of the Total Environment, 648, pp. 582–600.

Pomiès, M. *et al.*, 2013: *Modelling of micropollutant removal in biological wastewater treatments: A review,* Science of the Total Environment. 443, pp. 733–748.

Rivera-Utrilla, J. *et al.*, 2013.: *Pharmaceuticals as emerging contaminants and their removal from water. A review*, Chemosphere. 93(7), pp. 1268–1287.

Tadkaew, N. *et al.*, 2011: *Removal of trace organics by MBR treatment: The role of molecular properties*, Water Research. 45(8), pp. 2439–2451.

Verlicchi, P. and Zambello, E., 2015: *Pharmaceuticals and personal care products in untreated and treated sewage sludge: Occurrence and environmental risk in the case of application on soil - A critical review,* Science of the Total Environment, 538, pp. 750–767.

Watkinson, A. J., Murby, E. J. and Costanzo, S. D., 2007: *Removal of antibiotics in conventional and advanced wastewater treatment: Implications for environmental discharge and wastewater recycling*, Water Research, 41(18), pp. 4164–4176.

WET Center, 2016: *WET Center Pharmaceutical PNEC list*. Available at: http://www.nsfwetcenter.org/wp-content/uploads/2016/10/WET-Center-Phamaceutical-PNEC-list-3.pdf (Accessed: 15 October 2018).

Yuan, S. *et al.*, 2013: *Detection, occurrence and fate of 22 psychiatric pharmaceuticals in psychiatric hospital and municipal wastewater treatment plants in Beijing, China*, Chemosphere, 90(10), pp. 2520–2525.

Zhang, D. *et al.*, 2014: *Removal of pharmaceuticals and personal care products in aquatic plant-based systems: A review,* Environmental Pollution. 184, pp. 620–639.

Ako efektívne sú odstraňované mikropolutanty na čistiarňach odpadových vôd?

Lucia Ivanová

Anotácia
Cieľom tohto príspevku bolo určiť účinnosť odstraňovania liečiv na jednej z ČOV v Bratislave. Polovica liečiv identifikovaných v odpadových vodách je na ČOV odstraňovaná v účinnosťou viac ako 75 %. Väčšina liečiv bola odstraňovaná z odpadovej vody pomocou biodegradácie. Avšak fexofenadín, verapamil, sertralín, citalopram, amitriptylín a alfuzosín boli odstraňované pomocou sorpcie. Výsledky hodnotenia rizika pre životné prostredie poukázali na antibiotiká ako na potenciálne riziko pre životné prostredie.

Kľúčové slová: biodegradácia, čistiareň odpadových vôd, sorpcia

1 Úvod

Počas posledných desaťročí vzrástol záujem o liečivá, výrobky osobnej starostlivosti a endokrinné disruptory ako o potenciálne bioaktívne chemické látky v životnom prostredí. Tieto látky sú do životného prostredia neustále privádzané a ich bežné koncentrácie sú nízke, avšak môžu ovplyvniť kvalitu vody a majú potenciálny vplyv na zdroje pitnej vody, ekosystém a ľudské zdravie. Prítomnosť týchto látok v životnom prostredí bola len nedávno kvantifikovaná a bolo uznané, že sú potencionálne nebezpečné pre ekosystém. Táto skutočnosť prinútila Európsku úniu, aby vo svojom Vykonávacom rozhodnutí komisie (EÚ) 2015/495 z 20. marca 2015 zaradila do zoznamu sledovaných látok prvé farmaceuticky aktívne látky (diklofenak, 17α-etinylestradiol, 17ß-estradiol, estrón, erytromycín, klaritromycín a azitromycín) s cieľom zhromaždiť údaje z monitorovania a potvrdiť rizikové vlastností týchto látok.
Jedným z bodových zdrojov mikropolutantov do životného prostredia sú čistiarne odpadových vôd (ČOV). Čistiareň odpadových vôd pozostávajúca z primárneho čistenia založeného na fyzikálno-chemickom odstraňovaní zlúčenín a sekundárneho čistenia s biologickým reaktorom s aktivovaným kalom má obmedzenú kapacitu na odstraňovanie liečiv z odpadových vôd. Medzi hlavné mechanizmy odstraňovania mikropolutantov v systémoch s aktivovaným kalom patria biologický rozklad (biodegradácia), sorpcia na kal a vyprchávanie (stripping a odparovanie z povrchu systému). Avšak pre väčšinu mikropolutantov sú stripping a odparovanie z povrchu systému zanedbateľné, nakoľko Henryho konštanta by musela byť väčšia ako 100 $Pa.m^3/mol$. V procese biodegradácie sú znečisťujúce látky premieňané na látky s nižšou molekulovou hmotnosťou resp. úplne mineralizované na CO_2 a H_2O, kým mechanizmy odstraňovania polutantov pomocou sorpcie a vyprchávania sú založené na fázovej premene mikropolutantov (do dosiahnutia ich rovnovážnej koncentrácie).
Cieľom tohto príspevku je určiť účinnosť odstraňovania liečiv na jednej z ČOV v Bratislave a identifikovať, či zlúčeniny sú odstránené pomocou sorpcie alebo pomocou biodegradácie. Záver príspevku je venovaný hodnoteniu rizika pre životné prostredia pre vybrané liečivá.

2 Materiály a metódy

Na určenie účinnosti odstraňovania liečiv na ČOV bola prevedená LC-MS/MS analýza vzoriek z prítoku na ČOV, odtoku z ČOV a z kalu podľa Golovko *et al. (*2016) a Lindberg *et al.* (2014). Z koncentrácií liečiv v týchto vzorkách bola určená účinnosť odstraňovania liečiv na ČOV a bolo určené, do akej miery sa na odstraňovaní liečiv podieľa sorpcia a biodegradácia. Takisto bol prevedený výpočet rizikového kvocientu (RQ) pre najhorší možný scenár na základe prognózovanej koncentrácie nulového účinku (PNEC) z hodnôt dostupných v literatúre a na základe priemernej koncentrácie liečiv v odtoku z ČOV.

3 Výsledky a diskusia

Pomocou LC-MS/MS analýzy bolo analyzovaných 93 liečiv a drog a z toho 36 liečiv bolo identifikovaných na prítoku nad detekčným limitom. Tieto zlúčeniny boli kvôli prehľadnosti rozdelené do 6 skupín a to konkrétne analgetiká a antiflogistiká, antibiotiká, antihistaminiká, látky pôsobiace na kardiovaskulárny systém, látky pôsobiace na centrálny nervový systém a ostatné liečivá.
Pre skupinu analgetík a antiflogistík bola účinnosť odstraňovania liečiv v rozsahu od 35 do 95 %. Všetky látky z tejto skupiny boli prevažne odstraňované z odpadovej vody pomocou biodegradácie. Podobne aj antibiotiká boli z vody odstraňované len pomocou biodegrádacie. Ich účinnosť odstraňovania bola v rozsahu 25 až 93 %, pričom vo všeobecnosti vyššia účinnosť odstránenia bola určená pre makrolidové antibiotiká. Látky zo skupiny antihistaminík boli z odpadovej vody odstraňované v rozsahu od 47 do 89%, pričom sorpcia predstavovala významný mechanizmus odstraňovania pre fexofenadín. Všetky ostatné zlúčeniny z tejto skupiny boli prioritne odstraňované pomocou biodegradácie. Najviac sledovaných liečiv bolo zo skupiny látok pôsobiacich na kardiovaskulárny systém. Väčšina zlúčenín (8 z 12) mala účinnosť odstraňovania viac ako 90 %. Ostatné zlúčeniny boli odstraňované z odpadovej vody s účinnosťou v rozsahu od 52 do 75 %. V prípade verapamilu sorpcia predstavovala jediný mechanizmus odstraňovania tejto látky z odpadovej vody. Ďalšou skúmanou skupinou látok boli látky pôsobiace na centrálny nervový systém, pričom účinnosť odstraňovania týchto látok bola v rozsahu od 33 do 100 %. Len pomocou sorpcie z odpadovej vody z tejto skupiny látok boli odstránené sertraline, citalopram a amitriptylín. V poslednej skupine boli zaradené 3 liečivá a to konkrétne glimepirid s účinnosťou odstraňovania na ČOV 98 %, kodeín s účinnosťou odstraňovania na ČOV 69 % a alfuzosín s účinnosťou odstraňovania na ČOV 60 %. Z tejto skupiny látok bola sorpcia hlavným mechanizmom odstraňovania z odpadovej vody len pre alfuzosín.
Na pochopenie potencionálneho rizika spojeného s výskytom liečiv v odtoku z ČOV bol určený rizikový kvocient. Zlúčeniny boli rozdelené na základe tohto kvocientu na zlúčeniny s minimálnym rizikom pre životné prostredie($RQ \leq 0{,}1$), zlúčeniny so stredným rizikom pre životné prostredie ($0{,}1 < RQ < 1$) a na zlúčeniny s vysokým rizikom pre životné prostredie ($RQ \geq 1$). Väčšina zlúčenín, pre ktoré bolo vykonané hodnotenie rizika pre životné prostredie predstavujú pre životné prostredie minimálne riziko. Avšak stredne vysoké riziko pre životné prostredie predstavujú sulfametoxazol a klaritromycín a vysoké riziko pre životné prostredie predstavuje azitromycín.

4 Záver

V tomto príspevku bola zhrnutá účinnosť odstraňovania pre 36 liečiv vyskytujúcich sa v odpadových vodách. Polovica liečiv identifikovaných v odpadových vodách je na ČOV odstraňovaná v účinnosťou viac ako 75 %. Väčšina liečiv bola odstraňovaná z odpadovej vody pomocou biodegradácie. Sorpcia predstavovala hlavný mechanizmus odstraňovania pre fexofenadín, verapamil, sertralín, citalopram, amitriptylín a alfuzosín, čo môže predstavovať problém v prípade použitia kalu na poľnohospodársku pôdu. Zároveň je potrebné hľadať účinné metódy na odstraňovanie antibiotík z odpadovej vody,

nakoľko výsledky hodnotenia rizika pre životné prostredie poukázali na antibiotiká ako na potenciálne riziko pre životné prostredie.

5 Použitá literatúra

Golovko, O. *et al.*, 2016: *Development of fast and robust multiresidual LC-MS/MS method for determination of pharmaceuticals in soils*, Environmental Science and Pollution Research. 23(14), pp. 14068–14077.

Lindberg, R. H. *et al.*, 2014: *Occurrence and behaviour of 105 active pharmaceutical ingredients in sewage waters of a municipal sewer collection system*, Water Research, 58, pp. 221–229.