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THE REMOVING OF SELECTED PHARMACEUTICALS ON WWTP IN THE CZECH REPUBLIC

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In this article, the results of three years monitoring of selected pharmaceuticals (diclofenac, ibuprofen, carbamazepine, salicylic acid, clofibric acid) in the wastewaters of the Czech Republic are presented. The monitoring was performed on selected Wastewater Treatment Plants (WWTP) with various treatment technology and designed capacity. The concentrations and treatment efficiency of these substances were observed in various profiles of each WWTP, including influent, mechanical pretreatment, biological treatment, effluent. The main processes of removing selected pharmaceuticals during wastewater treatment are discussed. These results are used for design wastewater treatment technology with improved treatment efficiency of these substances.

Keywords: pharmaceuticals, wastewater, wastewater treatment, treatment efficiency.

Introduction

The relative importance of common types of pollutions in wastewaters such as easily biodegradable organic carbon, nitrogen or phosphorus is slightly decreasing. This situation is caused by reconstruction and intensification of many Wastewater Treatment Plants (WWTP), which could provide better and more efficient removing of these substances. Therefore the presence of specific pollutants in wastewaters is now in attention [1]. These substances can negatively influence not only water ecosystems, but in case of contaminating drinking water sources [2], even the human health. Part of these specific pollutants is substances commonly described as PPCP (pharmaceuticals and personal care products) [3]. Pharmaceuticals and their metabolites leave the human body in wastewaters and only some of frequent ones are successfully degraded by microbial communities. The concentrations of many other substances are practically the same on the effluent as in the effluent to the WWTP. We can also predicate that consumption of pharmaceuticals will be rising. New, these days unknown substances will also occur in the future. For that reasons, the successful removing of these substances from wastewaters seems to be very important these days. Therefore a research project focused on monitoring of these substances in wastewaters of the Czech Republic was launched. The main goals of this project are to describe the concentrations of selected substances in the wastewaters and the treatment efficiency on classic mechanical biological WWTP. On the basis of these findings the main issue is to describe and verify the most suitable technologies on WWTP for removing these substances.

This article summarizes the results of monitoring selected pharmaceuticals on four WWTP in the Czech Republic. The treatment efficiency of these substances is described and main treatment processes are discussed. These observed results are discussed with findings published by other authors. The possible technologies for improving of treatment efficiency of these substances are mentioned.

Experimental

These days a lot of pharmaceuticals occur in the water environment. Therefore five main representatives were selected for detailed monitoring. These substances were chosen on the basis of previous research projects about pharmaceuticals consumption (diclofenac, ibuprofen, carbamazepine, salicylic acid, clofibric acid) in the Czech Republic [4]. These substances represent most frequent drugs used in the Czech Republic.

Four WWTP with various treatment technology and designed capacity were chosen for monitoring of selected substances. The list of WWTP is described in the Table 1. These WWTP represents typical wastewater treatment technologies used in the Czech Republic.

The codes A to D were assigned for better orientation in the results. The abbreviation PE means population equivalent, which is commonly used as the indicator of the WWTP size. One PE means 60g BOD per day in the influent.

During the years 2010 – 2012, seventeen series of samples were collected from selected WWTP. Two series were done on WWTP A and five on WWTP B, C and D. Each series of samples included profiles as influent, mechanical pretreatment, biological treatment (denitrification, and nitrification) and effluent. The samples were collected as a spot sample. The profiles denitrification and nitrification were sampled as a wastewater and activated sludge mixture, where the activated sludge was settled down.

Table 1. The list of the observed WWTP

WWTP	Range of PE	Technological scheme
A	over 80 000	Mechanical-biological WWTP with biological nitrogen and phosphorus removal, anaerobic sludge stabilization.
B	10 000 – 50 000	Mechanical-biological WWTP with bio-filters, chemical precipitation aerobic sludge stabilization.
C	50 000 – 80 000	Mechanical-biological WWTP with biological nitrogen and phosphorus removal, anaerobic sludge stabilization
D	10 000 – 50 000	Mechanical-biological WWTP (carrousel type) with biological nitrogen removal, aerobic sludge stabilization.

Samples for determination of pharmaceuticals were filtered through cellulose membrane filters (porosity 0,45 μm) and after addition of mixture of internal standards 5 ml was preconcentrated by on-line SPE on Hypersil Gold 20x2,1 columns. For the entire determination method of LC/MS was used on liquid chromatograph Agilent 1200 RR equipped by binary and isocratic pumps, degasser, termostated autosampler, termostat of columns and by mass detector Applied Biosystems 4000 Q Trap with the triplicated quadrupole. Zorbax XDB 50, 50x4,6 mm, 4 μm column was used, with the mobile phase methanol/water acidified 0,2% of acetic acid in the gradient elution. The mass detection was done by an electrospray in the negative (ESI) and positive (ESI+) modes. For the input to SPE (5 ml volume) the Aspec GX-271 instrument (Gilson) was used.

Results and discussion

The results were summarized into Tables 2 – 4. The total treatment efficiencies of selected substances on the observed WWTPs are described in the Table 2. The best removing efficiency of observed substances was reached for Ibuprofen. For this substance, average removal efficiency 98% was observed. The removal ratio was also very stable; results of WWTP A, C and D are also very stable with no variation. The only exception is WWTP B, where treatment efficiency even about 50% occurred. Similar results were detected for salicylic acid. The removal efficiency was in the interval of 90 – 98% with one exception, when during sample No. 4 at WWTP B only 55% removal efficiency was founded. It can be assumed, that these relatively low treatment efficiencies of ibuprofen and salicylic acid were caused by unstable biological processes which occurred during taking sample No. 4. In that case even low treatment efficiency of COD and especially ammonia nitrogen were observed.

Table 2. The total treatment efficiency of observed substances

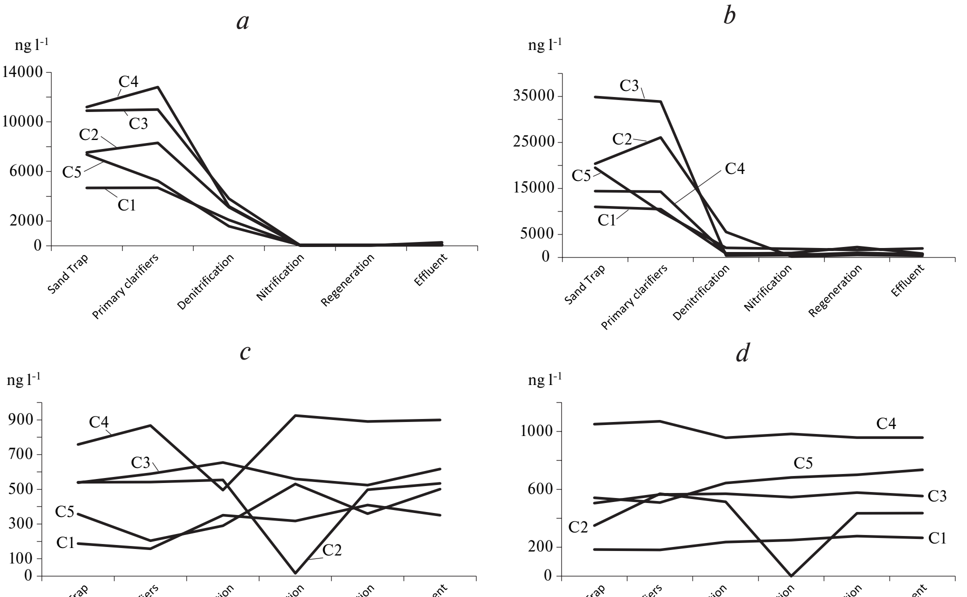
WWTP	No. of Sample	Clofibric Acid	Diclofenac	Ibuprofen	Salicylic Acid	Carbama-zepine-
[%]						
A	1	x	20	98	95	-26
	2	x	-118	99	96	0
B	1	≥ 59	-31	94	98	-51
	2	≥ 57	-8	98	98	-18
	3	≥ 52	-46	95	92	-16
	4	x	-58	50	55	-367
	5	x	-28	64	95	-14
C	1	x	-88	99	93	-44
	2	2	1	96	98	-24
	3	≥ 54	-15	99	98	-10
	4	x	-19	99	95	9
	5	x	-40	98	90	-36
D	1	≥ 66	33	99	97	27
	2	≥ 35	3	99	98	14
	3	x	-25	98	99	-2
	4	x	-19	98	95	3
	5	x	-78	98	96	9

According to data obtained from monitoring, diclofenac and carbamazepine are substances which are resistant to biological treatment. In a few cases maximal treatment efficiency 33% for diclofenac and 27% for carbamazepine was reached. More often the increase of the concentrations for these substances during wastewater treatment was observed. As mentioned in the introduction, these substances leave human body in various forms (original substance, metabolites).

The diclofenac and carbamazepine are commonly known for slow deconjugation of metabolites to the original substance. While average hydraulic retention time on common WWTP is approximately several hours, this is the sufficient time for that deconjugation. Because we are not able to measure the metabolites of these substances in the influent the concentrations are "rising" at the effluent.

The concentrations of the clofibric acid in the wastewaters were very variable. Concentrations under the detection limit in the influent and also effluent was observed on WWTP A. On the other three WWTP various concentrations of clofibric acid were observed. The removal ratio for this substance was approximately 55%.

Figure shows typical progress of concentrations during wastewater treatment. Ibuprofen and salicylic acid are removed during biological treatment, while diclofenac and carbamazepine are not biologically degradable and the concentrations in the effluent are almost the same as in the influent.



The progress of concentrations of observed substances during biological treatment on WWTP C: ibuprofen (a), salicylic acid (b), diclofenac (c), carbamazepine (d).

The Table 3 summarizes the removal efficiency for mechanical pre-treatment (profiles influent, sand catcher, primary clarifiers) and biological treatment (profiles denitrification, nitrification and effluent). These results show that observed substances are eliminated almost in the biological stage and mechanical pre-treatment does not plays any significant role.

Table 3. The treatment efficiency on mechanical and biological stage of observed substances

WWTP No. of sample	Profile	Clofibric Acid	Diclo-fenac	Ibu-profen	Salicyl Acid	Carba-mazepine
		[%]				
A1	Mech. Pre-reatment	x	36	28	32	5
	Biological treatment	x	-24	98	92	-33
A2	Mech. Pre-reatment	x	-21	6	13	11
	Biological treatment	x	-79	99	96	-11
B1	Chem. precipitation	31	-21	46	80	-34
	Biofilters	≥ 41	-8	90	89	-12
B2	Chem. precipitation	5	-35	7	28	-5
	Biofilters	≥ 55	20	98	97	-13
B3	Chem. precipitation	17	-11	6	95	6
	Biofilters	≥ 42	-32	94	91	-24
B4	Chem. precipitation	x	-18	-10	38	-41
	Biofilters	x	-34	55	28	-232
B5	Chem. precipitation	x	-32	28	47	-11
	Biofilters	x	3	51	91	-3
C1	Mech. pre-treatment	x	16	0	5	2
	Biological treatment	x	-122	99	92	-46
C2	Mech. pre-treatment	-16	0	-10	-28	-63
	Biological treatment	15	2	97	99	24
C3	Mech. pre-treatment	7	-10	-1	3	-12
	Biological treatment	≥ 51	-5	99	98	2
C4	Mech. pre-treatment	x	-15	-14	1	-2
	Biological treatment	x	-4	99	95	11
C5	Mech. pre-treatment	x	43	28	49	6
	Biological treatment	x	-146	98	80	-45

The difference of removal efficiency of observed substances during denitrification and nitrification processes is summarized in the Table 4. The results of WWTP A, B and C indicate that for successful removing ibuprofen and salicylic acid stable nitrification processes is the main factor. The WWTP D is carrousel type technology and denitrification and nitrification is not consequent but simultaneous. Therefore, these results are not fully comparable with WWTP A to C.

Table 4. The treatment efficiency of denitrification and nitrification of observed substances

WWTP No. of sample	Profile	Clofibric Acid	Diclo-fenac	Ibuprofen	Salicyl Acid	Carba-mazepine
		[%]				
A1	Denitrification	x	32	49	76	-1
	Nitrification	x	-78	96	96	-1
A2	Denitrification	x	-55	53	69	-8
	Nitrification	x	12	96	87	-5
B1	Anoxic biofilter	x	-3	16	84	-9
	Oxic biofilter	x	-5	87	29	-3
B2	Anoxic biofilter	32	31	47	53	4
	Oxic biofilter	≥ 34	-16	97	94	-17
B3	Anoxic biofilter	x	5	49	62	-13
	Oxic biofilter	x	-39	89	77	-10
B4	Anoxic biofilter	x	-5	52	71	-17
	Oxic biofilter	x	-27	5	-148	-184
B5	Anoxic biofilter	x	8	33	72	1
	Oxic biofilter	x	-6	26	67	-4
C1	Denitrification	x	-122	55	92	-30
	Nitrification	x	9	98	-16	-6
C2	Denitrification	27	-2	63	79	10
	Nitrification	7	97	99	97	99
C3	Denitrification	≥ 51	-11	65	99	-1
	Nitrification	x	15	99	-14	4
C4	Denitrification	x	43	75	94	11
	Nitrification	x	-87	98	23	-3
C5	Denitrification	x	-42	70	79	-27
	Nitrification	x	-83	95	11	-6
D1	Denitrification	x	44	99	98	25
	Nitrification	x	47	99	95	26

Table 4. (Contd.)

D2	Denitrification	x	16	97	92	15
	Nitrification	x	-4	99	98	15
D3	Denitrification	x	10	96	98	-2
	Nitrification	x	-10	99	99	-4
D4	Denitrification	x	-13	94	96	8
	Nitrification	x	-6	99	96	12
D5	Denitrification	x	-35	96	95	9
	Nitrification	x	-27	99	95	6

The main factors of removing PPCP on WWTP. Hydraulic retention time (HRT) and sludge retention time (SRT) are the key parameters of activation treatment plants. Generally, activation process effect on drug elimination increases with increasing retention time (HRT) and especially with increasing sludge retention time (SRT) – it is explained, besides longer reaction time, by higher diversity and adaptation of sludge microbial communities.

Removal efficiency over 90% is stated for most pharmaceutics at quite standard SRT about 15 – 20 days, except carbamazepine, clofibric acid and diclofenac [5 – 7] - some standard WWTP show surprisingly low elimination of e.g. degradable ibuprofen [8]. Experimental data on the influence of SRT do not always match with the real processes in wastewater treatment plants – under regular operation conditions activation process efficiency could vary with fluctuating sludge retention time during storm events [9]. Zhang et. al. [10] summarized the data dealing with influence of SRT in activation treatment plants on particulary problematic drugs carbamazepine and diclofenac. Carbamazepine was resistant in extent of total SRT (100 days), diclofenac showed maximum (50% elimination) in the segment from 20 to 50 days. carbamazepine unlike clofibric acid and diclofenac, which concentrations after passing WWTP decrease at least in some cases, is not degraded and increase in its concentrations is found along WWTP [7, 11, 12]. Slower deconjugation into determinable parent substance is the partial explanation, but already input evaluations of carbamazepine do not match with the assumptions based on average consumption and number of people connected to WWTP [13].

Membrane reactors are specific for their technical capabilities maintain high SRT. That corresponds to a statistically significant increase in elimination of drugs as compared with standard activation processes [14 – 17]. Also activation processes with enhanced nutrient removal are more efficient in drug elimination [14, 18, 19].

Effect of mechanical pretreatment ondrug elimination is generally considered to be insignificant, except for the gradual transformation of estrone to estradiol.

Special processes aimed at elimination of drugs in the secondary treatment of wastewater are still working as experimental operation rather than real operation. Salgado et al. [20] conducted experiments with disinfection of wastewater effluent from a wastewater treatment plant by UV radiation. The system was effective on clofibric acid and diclofenac (wastewater after passing through WWTP), it was not effective on ibuprofen elimination. Serrano et al. [21] noted a positive influence of dosing of powdered activated carbon for removal of carbamazepine. On the contrary, using $FeCl_3$ as the coagulant for the removal of drugs has proved ineffective. Okuda et al. [19] found positive effect of ozonation on drug elimination, technologies such as coagulation, sedimentation and sand filtration, chlorination and UV disinfection had any effect.

Conclusions

These results gained during three years of monitoring of selected substances comply with results published by other authors. It was confirmed that mechanical pre-treatment do not plays any significant role in removing for all observed substances. Ibuprofen and salicylic acid are highly biodegradable in WWTP, but even 99% treatment efficiency significant concentrations of these substances can be found in the WWTP effluents. The main factors of high removal efficiency are hydraulic retention time and sludge age. The diclofenac and carbamazepine are not removable on common mechanical biological WWTP. Therefore for sufficient removing of these substances, new technologies as ozonation or UV radiation must be involved as a part of tertiary treatment. Low concentrations of clofibric acid in the influents were detected. This is not corresponding with estimated consumption in the Czech Republic. However explanation of this situation could be the fact that the drugs based on this substance were substituted.

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Received 07.02.2014