УДК 628.35

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MONITORING OF MIKROPOLUTANTS PRESENT IN SLUDGE WATERS PRODUCED ON MUNICIPAL WASTEWATER TREATMENT PLANTS

INTRODUCTION

Environment is inevitably altered by human activity. Mineralization of this influence is in present time public effort. Progress in production and also in area of waste management have considerable impact on the penetration of hazardous materials into environment around us.

Over the last few years, however, progress has been made in the field of analytical chemistry to such an extent that we were able to record the quantities of the order of tens of nanograms, penetrating the recipients of WWTP. The newly recorded source of contamination of surface water produces small but dangerous amounts of micropollutants. This pollution can cycle through the water to penetrate to the source of drinking water for agricultural land and food chain to humans (Fick, J. et al., 2009).

The sludge is generated as biomass growing from the organic fraction of the waste water rich in a source of carbon, nitrogen and phosphorus. These substances are converted during the cleaning processes into the cells and organelles of microorganisms. In the WWTP system should always be a certain amount of microorganisms. This amount is maintained with sludge wasting of excess sludge. Stabilized sludge is mechanically dewatered and exported for disposal. The sludge water is thus released by mechanical or gravitational dewatering of sludge. Sewage water is discharged ahead of cleaning processes where there is mixing it with influent.

Since not even modern wastewater treatment plants are currently designed to degrade micropollutants, they pass through the process and entering recipients. Micropollutants concentrated in the sludge penetrate through the water and wastewater into surface waters. Gomez et al. presented the results wherein a tramadol urban waste water reached up to 1129 $ng.l^{-1}$ and 757 $ng.l^{-1}$ in the wastewater discharged from WWTP (Gomez et al., 2012). Among the biggest sources of pharmaceuticals in waste water include hospitals and the pharmaceutical industry itself (Berto, J. et al. 2009).

Among monitored micropollutants currently belong pharmaceuticals, drugs and their metabolites. A serious problem for the environment present psychoactive substances affecting fish behavior through changes in brain chemistry and nervous system and hormonal system. Test compounds are commonly found in high concentrations in the effluent from sewage (Gomez et al., 2012). Drugs and metabolites can have a similar effect as psychoactive substances (Brodin, 2013).

Antibiotics are a major problem already in contact with micro-organisms in the sewers and then in treatment plants itself. However, residues of antibiotics penetrate further into water bodies where they operate. The main problem with antibiotics is their potential to induce resistance of bacterial strains. This resistance can be further disseminated through various mechanisms of transmission and cause serious complications in the treatment of diseases (Birošová, 2013, Gyles, 2014).

Nowadays we know several effective methods of removing this pollution from wastewater, among other oxidation reactions headed by Fenton reaction, but also ongoing research into reactive particles such as Ferrates application or boron-doped electrodes. These methods have had modest success in laboratory conditions, but their practical application still has a long journey (Mackuľak, 2014).

EXPERIMENTAL PART

Sample analysis

Spot samples were collected on selected WWTP and right after frozen and transported to laboratory. In laboratory were samples melted, every sample was homogenized and

filtered with GFC, 0,45 μm filter. To 10 ml of sample it was added isotope-marked internal standards. Samples altered with this method were analyzed by SPE HPLC method in tandem with hybrid quadruple (Orbitrap) with highly sensitive mass spectrometer. This analytical method is highly sensitive and able to capture pharmaceuticals, drugs and its metabolites in wastewaters in very low concentrations (Fedorova, 2013)

Sample collection

Samples of sludge water were collected from dewatering processes on WWTP, influents and effluents were collected in 24-hours intervals where every 30 minutes were collected proportional sample from influent and effluent.

RESULTS AND DISCUSSION

Medicines and drugs have the ability of sorption to the sludge generated in the treatment plants. As long as these sludge (such as raw) is used in the production of biogas, some types of pharmaceuticals, drugs or their metabolites have ability to penetrate into anaerobic processes, where they may undergo biodegradation, sorption or just accumulation. Subsequently, when dewatering occurs, water from this process is rich of these compounds because of concentrating, with the result of concentrations above 100 $ng.l^{-1}$. The often analyzed compounds or psychoactive substances in the sludge water include tramadol, venlafaxine or methamphetamine. Also, dominant metabolite of nicotine - cotinine most concentrated one of the compounds (Table 1).

Table 1 - The measured amount of tramadol, venlafaxine, methamphetamine and cotinine in sludge water of urban waste water treatment plant Piestany, Nitra, Petržalka and Vrakuňa.

		Piešťany	**Nitra**	**Vrakuňa**	**Petržalka**
Tramadol	[$ng.l^{-1}$]	197	604	840	1239
Venlafaxine	[$ng.l^{-1}$]	137	244	589	481
Methamphetamine	[$ng.l^{-1}$]	456	295	1114	427
Cotinine	[$ng.l^{-1}$]	28440	703	5477	531

Table 2 - Measured amounts of selected antibiotics in the various stages of cleaning process of the WWTP Petržalka

	Influent	**Mechanically treated water**	**Sludge water**	**Effluent**
	$ng.l^{-1}$	$ng.l^{-1}$	$ng.l^{-1}$	$ng.l^{-1}$
ciprofloxacin	1910	626	543	96
azitromycin	1800	1390	1090	919
claritromycin	2750	1020	479	684
sulfapyridine	531	136	178	125
penicillin V	< 2,1	< 2,1	< 1,7	< 2

The other way to the particularly psychoactive compound to enter environment from stabilization processes is their application on fields, either directly or subsequently by the production of compost (compost Processing occur by temperature of 80 ° C).

Antibiotics present in the cleaning process results in the formation of resistant bacterial strains. The most represented antibiotic at the influent to the treatment plant in Petržalka was clarithromycin. Its concentration in the effluent, however, amounted to the second highest. Compared to the other, the concentration of azithromycin in the effluent from WWTP was highest. With a concentration value of 919 $ng.l^{-1}$ in effluent has a concentration comparable to the concentration of the sludge water, and half as much as in influent. Ciprofloxacin and sulfapyridine were relatively well removed and WWTP effluent concentrations represented 96 and 125 $ng.l^{-1}$ (Table 2).

CONCLUSION

As apparent from the above values, the issues of micropollutants have to be addressed in the future. The first step to successfully reduce penetration of micropollutants into recipients of our wastewater treatment plants is accurate identification of roads by which micropollutants cross through the processes of cleaning and stabilization.

At the same time it will be necessary to identify the level of risk that these substances carry with them and understanding their effects in the aquatic ecosystems and soils.

By focusing on risk such as microbial resistance and transfer of resistance among bacterial strains we manage to minimize the possibility of penetration of these dangerous pathogens in the environment and can thus increase the effectiveness of currently used antibiotics.

ACKNOWLEDGEMENTS

This thesis formation was supported by the Agency for support of science and research APVV-0122-12.

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УДК 628.16.066.1

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ТЕОРЕТИЧНІ АСПЕКТИ НАПІРНОЇ ФЛОТАЦІЇ МАЛОКАЛАМУТНИХ КОЛЬОРОВИХ ВОД

Введення. За теперішнього часу в Україні практично всі водні об’єкти зарегульовані. Внаслідок цього, показники якості вихідної води мають низькі значення каламутності (менш ніж 50 мг/л). У зв’язку з відсутністю руху води та під дією сонячних променів, а також через скид стічних вод і поверхнево-зливогого стоку утворюються органічні сполуки, які зумовлюють кольоровість поверхневих вод [1]. У багатьох випадках значення кольорово-