REMOVAL EFFICIENCY OF ARTIFICIAL SWEETENERS IN WASTEWATER TREATMENT PLANTS IN SERBIA

E. Gvozdić [1], I. Matić Bujagić [2], T. Đurkić [3] and S. Grujić [3]

[1] *Innovation Centre of the Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia.*
[2] *Department of Environmental Engineering and Occupational Safety, Belgrade Polytechnic College, Academy of Applied Technical Studies Belgrade, Katarine Ambrozić 3, 11000 Belgrade, Serbia.*
[3] *University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia. (svetlana.grujic@tmf.bg.ac.rs)*

ABSTRACT

Artificial sweeteners have been recognized as high-priority emerging contaminants that cause great concern due to unknown environmental behavior and long-term ecotoxicological impact on water resources. Wastewater treatment plants are not designed to remove these pollutants and consequently they are continuously introduced into the aquatic environment. This paper describes investigation of four artificial sweeteners, highly abundant in urban wastewater, and their removal rate in wastewater treatment plants in Serbia, in order to assess the efficiency of the treatment to reduce their environmental inputs. For this purpose, influent and effluent wastewater samples from two treatment plants were extracted and analyzed using liquid chromatography–tandem mass spectrometry.

INTRODUCTION

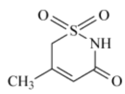
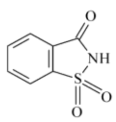
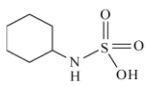
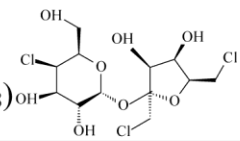
Artificial sweeteners are widely utilized as sugar substitutes in human diets and animal feeds due to their high-intensity sweetness and low caloric value [1]. Following ingestion, a large percentage of these compounds are excreted in an unchanged form [2]. As a result of wastewater effluents and untreated municipal wastewater discharges, traces of these substances have been reported in natural waters [1, 3]. Furthermore, with the increasing use of various artificial sweeteners, the long-term risks to human health and the environment resulting from continuous exposure to low levels of these compounds remain largely unknown. For that reason, artificial sweeteners are recently recognized as high-priority emerging contaminants [1]. Due to their high persistence, ubiquitous occurrence in aquatic ecosystems and incomplete removal in wastewater treatment plants (WWTPs), artificial sweeteners can be used as powerful tracers of sewage pollution [3]. Current wastewater treatments are a combination of physical, chemical and biological processes for the removal of different pollutants. However, even the most effective treatments have limited ability to completely remove all existing contaminants [3, 4]. As a consequence, WWTP effluents are a major point source of many environmental pollutants, including artificial sweeteners.

The aim of this work was to determine the levels of acesulfame, saccharin, cyclamate and sucralose in influent and effluent wastewater of two WWTPs in Serbia and their removal efficiency in order to evaluate the impact of the treatment on quality of the water resources. Due to high sensitivity and selectivity, liquid chromatography with tandem mass spectrometry (LC–MS/MS) is the method of choice for detection of traces of artificial sweeteners in complex wastewater samples.

METHODS

The physico-chemical properties of the selected artificial sweeteners are presented in Table 1.

Table 1. Chemical structures and physico-chemical properties of the selected artificial sweeteners: molecular weight (M_w), octanol-water partitioning coefficient (K_{ow}) and water solubility at 25 °C (WS)

Artificial sweetener (formula)	Chemical structure	M_w (g mol^{-1})	$\log K_{ow}$[a]	WS[a] (mg L^{-1})
Acesulfame ($C_4H_5NO_4S$)		163.1	–1.33	9.1×10^5
Saccharin ($C_7H_5NO_3S$)		183.1	0.45	789.2
Cyclamate ($C_6H_{12}NO_3S$)		179.2	–1.61	1.0×10^6
Sucralose ($C_{12}H_{19}Cl_3O_8$)		397.6	–1.00	2.3×10^4

[a] Source: ChemSpider database; http://www.chemspider.com/

Sewage influent as well as effluent samples were collected from two municipal wastewater treatment plants in Serbia, with the population equivalents of 25,000 (WWTP1) and 2,000 (WWTP2). Conventional treatment processes of the two treatment plants include primary precipitation coupled with secondary biological activated sludge treatment. Sampling was performed over a time range of 4 hours and composite samples were taken.

The wastewater samples were filtered through 1–3 μm glass fiber filters and prepared for the analysis using solid-phase extraction (SPE). In a SPE procedure, a 50 mL of the water sample, with pH adjusted to 3.0, was loaded onto Oasis HLB cartridge (200 mg/6 mL) from Waters, USA. Sweeteners were eluted with 10 mL of methanol and extract was evaporated and reconstituted to 0.5 mL.

LC analysis was performed using Dionex UltiMate 3000 HPLC system (Thermo Fisher Scientific, Waltham, US). The chromatographic separation was carried out on Luna® C8 (3.0 mm × 150 mm, 3 μm) column. Mobile phase consisted of (A) deionized water, (B) methanol and (C) 0.1 mol L^{-1} aqueous solution of ammonium acetate. The mass spectra were recorded by LTQ XL (Thermo Fisher Scientific) linear ion trap mass spectrometer using electrospray ionization (ESI) in the negative ionization mode.

RESULTS AND DISCUSSION

All investigated artificial sweeteners were found at high levels in influents of both treatment plants (up to 9631 ng L^{-1} for cyclamate), with WWTP1 showing much heavier wastewater burden reflecting the number of inhabitants in the investigated area (Table 2). For both WWTPs, very low removal efficiency of acesulfame was noted (19.8% and 0.3%, respectively). These results are in accordance with other authors who indicated that acesulfame, along with sucralose, was the most persistent sweetener in wastewater treatment [3, 4]. For this reason, both can be used as chemical markers for tracing municipal wastewater contamination in the aquatic environment. In our study, only WWTP2 showed low elimination rate of sucralose (21.4%), while WWTP1 was more efficient in sucralose removal (64.5%). The highest removal efficiency in both WWTPs was achieved for cyclamate (68.8 % and 94.1%, respectively). The results of similar studies showed that the highest removal rates were usually obtained for cyclamate and saccharin (up to 94%) [3, 4]. However, our results for elimination of saccharin showed that WWTP1 was less efficient (28.9%), whereas WWTP2 showed higher elimination potential (69.5%). Biodegradation is considered a key mechanism for elimination of artificial sweeteners in biological wastewater treatment, while sorption plays a minor role due to their high water solubility [1].

Table 2. Concentrations of artificial sweeteners detected in influents and effluents and removal efficiency (RE)

	Artificial sweeteners	Concentration ± SD (ng L^{-1}) Influent	Effluent	RE (%)
WWTP1	Acesulfame	5436 ± 176	4365 ± 225	19.8
	Saccharin	7080 ± 452	5033 ± 511	28.9
	Cyclamate	9631 ± 337	3009 ± 198	68.8
	Sucralose	7174 ± 111	2544 ± 178	64.5
WWTP2	Acesulfame	1600 ± 98	1596 ± 127	0.3
	Saccharin	3800 ± 301	1200 ± 117	69.5
	Cyclamate	1700 ± 88	100 ± 12	94.1
	Sucralose	1400 ± 95	1100 ± 85	21.4

CONCLUSION

The determined high levels of selected artificial sweeteners in both influent and effluent samples and low or incomplete removal in WWTPs indicate continuous contamination of the aquatic environment in Serbia with these substances. Only in the case of cyclamate, high removal rate was determined. Nevertheless, the results have confirmed importance and crucial impact of municipal wastewater treatment on the quality of the water resources and reduction of environmental inputs of the pollutants.

Acknowledgement

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract no. 451-03-9/2021-14/200287 and 451-03-9/2021-14/200135).

REFERENCES

[1] J. Luo, Q. Zhang, M. Cao, L. Wu, J. Cao, F. Fang, C. Li, Z. Xue, Q. Feng, Science of the Total Environment, 2019, 653, 1149–1160.
[2] A. G. Renwick, Xenobiotica, 1986, 16, 1057–1071.
[3] M. Scheurer, H.-J. Brauch, F. T. Lange, Analytical and Bioanalytical Chemistry, 2009, 394, 1585–1594.
[4] B. Subedi, K. Kannan, Environmental Science and Technology, 2014, 48, 13668–13674.