



“Gheorghe Asachi” Technical University of Iasi, Romania



HEAVY METAL BALANCE IN A HUNGARIAN MUNICIPAL SEWAGE TREATMENT PLANT

Gábor Gulyás*, Viktória Pitás, Árpád Kárpáti, Bence Fazekas,
Endre Domokos, Ákos Rédey

Pannon University, Institute of Environmental Engineering, H-8200 Veszprém, Egyetem Street 10

Abstract

The present study was undertaken to experimentally evaluate the heavy metal (HM) removal capacity of a municipal wastewater treatment plant (WWTP) as a kind of mass balance. The aim of the work was to find a water or sludge stream in the WWTP that could be treated separately for heavy metal removal to maximize the same efficiency of the whole treatment technology. Although literature says that the HM content of sewage accumulates in the sewage sludge, the experimental results showed no compliance with it.

The results obtained demonstrated that 85-95% of the inlet metal content was discharged into the recipient and only 5-15% was retained in the digested sludge in the studied plant. A few percentage of the metal content of the influent could only be measured in the primary and secondary sludge. Otherwise the metal concentration of these sludge streams was very similar. The reject water had an inconsiderable metal recycle in the technology, not more than 2-3% of the influent load. Approximately 2-10% of the HM inlet was removed by the sand trap.

The separate HM removal from the sludge streams seems to be inadequate since most of the HM load of the plant was finally discharged with the treated effluent to the receiver. This is the reason why the prevention of these contaminants' getting into the sewage is the most important task.

Key words: activated sludge, heavy metals, mass balance, municipal wastewater

Received: February, 2014; Revised final: August, 2014; Accepted: August, 2014

1. Introduction

Industrial sewage discharges entering the municipal WWTPs from metal refining and other industries are hazardous for the treatment technology because of their heavy metal (HM) content. That is why nowadays the HM removal from these discharges at the site of the waste production is strictly regulated. The next possibility for the removing the HMs from wastewater is the activated sludge process (ASP) of the POTWs (Lester, 1983). Mechanisms of HM removal in AS process are however not completely known yet ((Barakat, 2011; Karvelas et al., 2003). Even the inhibition effects of some metals for the specific microorganisms (MOs) are not properly known. That is why our study tried

to summarize the HM removal of an AS plant on the base of its detailed mass balance. Neither the influence of any technological parameters like oxygen supply, pH, sludge age, complexing agents etc. (Karvales et al., 2003; Özbegle et al., 2005), nor the microbial composition of the working biomass were examined in this study.

The most hazardous heavy metals are Cd, Cr, Hg, Pb, Zn, Ni and Cu. They pose a significant risk to the environment and public health (Yan et al, 2014). Therefore the removal of heavy metals from wastewater is very important.

Heavy metal sources can be the households and industries (Wang et al, 2006). Such industries are the mining, metal processing, cable making and microchip production (Moussa and Qdais, 2004;

* Author to whom all correspondence should be addressed: e-mail: g.gulyas.up@gmail.com; Phone: 003688624286

Martin-Lara et al., 2014). Cd, Cr, Pb and Hg are mainly originated in chemical-intensive industries (Barakat, 2011). Transport is also very critical field of heavy metal emission. Within transport the wearing of breaks, tyres and asphalts are the more pollutant sources (Sörme et al., 2002).

A quarter of a century later, Stephenson et al. (1987) and Karvelas et al. (2003) tried to overview the possibility of the removal of metals from sludge of the AS sewage treatment plants. They published rather different removal efficiencies referring to a lot of measurements all over the world. They concluded that about 70% of the Manganese and Copper load can be accumulated in the AS, while 50 – 60% of the Cr, Cd, Pb, Fe, Ni, Zn leave the plant and is discharged to the recipient with the treated effluent. It is well known, that some special forms of these HMs in the sludge or in the AS system are more critical than their total concentrations (Álvarez et al., 2002).

In this study the HM concentrations were measured in the different liquid and sludge streams of a Hungarian wastewater treatment unit treating municipal effluent relatively free of industrial metal discharges. On the base of these concentrations we calculated a total mass balance for the plant and checked the possibility of separate removal of some metal contaminants from the sludge residue to produce more valuable agricultural soil amendment

2. Material and methods

The studied ASP treats 13 000 m³ sewage daily. However, its nominal capacity is 21 000 m³/d which shows the system is considerably underloaded. It has proper digestion capacity for the primary and secondary sludge of the main stream. The measurement of HM concentrations besides the inflow and purified effluent in some mixed liquid streams and the final dewatered sludge was also conducted. From the material balance made with the help of these data it seemed possible to decide about the reality of the use of some separate heavy metal removal step in the treatment line. In order to make a valuable metal balance samples were taken several times in different daytime from the liquid, mixed sludge and dewatered sludge as well. The sampling points in the technology are shown in Fig. 1.

Samples 1-4 were collected during the whole day. Sampling was in every second hour, equalized, cooled down and stored as prescribed. Samples 5-8 were collected, when sludge pumping or dewatering was operated. These samples were stored for processing similarly. Frequency of sampling was once a week over three weeks. Samples 1-4 and 8 were composite samples, other samples (5-7) were grab samples.

The measurements were made after dissolution of metal content of the samples, with atomic adsorption spectrophotometer (AAS) of 8 metal contaminants. From these data the metal content of the sludge phases were calculated, with the suspended and total solid contents (SS and TS) of the

last four samples taken into account, supposing that dissolved heavy metal content of the liquid phase is equal with that of the treated effluent in samples 6 and 7 and with the metal content of the reject water in sample 8.

For measuring SS and TS content of the sludge containing samples (No. 6-8) MSZ 260/3-73 standardized method was used. Average daily amount of the reject water had to be calculated for the calculation of the material balance from these measured values as the flow is not measured in the plant. MSZ 260/3-73 was applied for the determination of the dissolved and suspended matter content. Suspended and dissolved materials were determined by vaporization of water content from homogenous and filtered sludge samples (at 105 °C). Organic and inorganic ratio of suspended solids were determined by the burning of solid material content at 600 °C.

Dissolution of the metals from the different samples was made by Mars 6 microwave digester. The temperature program of the digester was optimized in a previously published study (Gulyás et al., 2013). For addition of chemicals to digesting we followed the proposal of MSZ 1484-3 standard tricking to the quantities of samples as well. Before digestion 3 ml of 68 % HNO₃ and 9 ml of concentrated HCl was given to every 0,5 ml sample. During the microwave digestion of the sludge samples, the same heating program was used in each case. After the heating up (20 minutes) the digestion was done for 10 minutes on 180°C. After the digestion as above, and dilution according the prescriptions, the HM concentrations were measured with Thermo Scientific ICE 3000 Atomic Adsorption Spectrophotometer.

3. Results and discussion

During the study the samples were taken in three one week period. The 8 metals monitored were Cd, Co, Mn, Ni, Cr, Cu, Fe, Pb. We measured the weekly equalized samples stored in refrigerator and measured on the next weeks which means that measurement were also made three times. The average metal contents for the whole measured period can be seen in Table 1. The detection limits of each heavy metal are 0.001 mg/L in ICE 3000 Atomic Adsorption Spectrophotometer.

It can be seen from Table 1 that there was no Pb over detection limit at all in the influents of the WWTP. They had very low Cd concentration, in average 0.03 mg/L. Mn and Ni has a bit higher concentrations in the range of 0.08-0.15 mg/L. Cobalt had similar concentration in average like Mn and Ni had, but in one of the three samples there was 0.20 mg/L of it. Cobalt was just in a bit higher concentration in the sewage than Mn and Ni. Its concentration varied in the samples in the range of 0.10-0.30mg/L. The content of Cu was however stable somewhere around 0.20 mg/L. This could not be surprising as we measured similar values in the

last few years at this plant. The Fe had the highest concentration in the inflow and it remained similar to that of the other metal contaminants in the outflow from the plant. To make the heavy metal mass balance of the plant we needed the average flow data of the streams sampled. To make the mass balance for the HM in the process the flow rates and the sludge production had to be taken into account. As the hydraulic retention time (HRT) in the plant was more than one day and the sludge age was near 20 days we used average figures for the calculation of the balance. The same was used for the primary and secondary sludge streams, as their take-away was not continuous, but the material we examined was properly equalized. The average daily quantities of the streams can be seen in Table 2.

There were some parameters required to the calculation which were not measured in the plant. Such parameter was the average daily quantity of the reject water, which we calculated from the SS concentration of the digested sludge stream entering

the dewatering centrifuge and that of the dewatered digested sludge. The quantity of the dewatered digested sludge was not measured so it was calculated from the volume of the sludge transported from the centrifuges to the solar drying part of the plant and its average dry solid content. This resulted in a negligible mistake since the dissolved material content of the sludge water or the reject water was low enough.

From Tables 1 and 2 it cannot be seen, but flow quantities and concentrations were changing in a wide range. Differences in the daily inflows ranged to $\pm 22\%$, while in their HM content changed even between $\pm 31\%$. In the sludge streams the difference of the HM concentrations was far smaller than expected after the equalization. This is why the calculation of the balance was made with the average figures. With the concentrations and daily flows heavy metal contents in these sewage and mixed liquid flows could be calculated (Table 3).

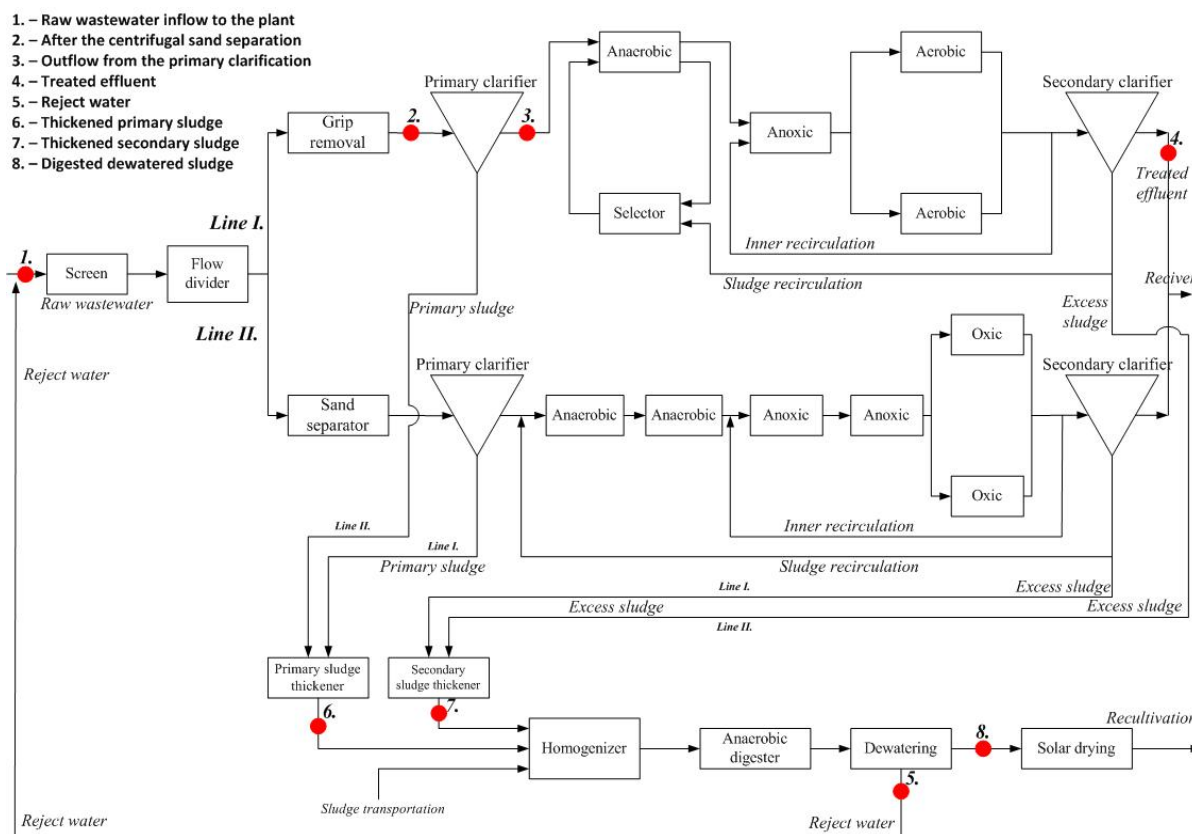


Fig.1. The technology and the sampling points for checking HM concentrations

Table 1. The total heavy metal concentrations of the streams of the ASP

Samples	Cd	Co	Mn	Ni	Cr	Cu	Fe	Pb
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Raw wastewater	0.02	0.17	0.12	0.12	0.19	0.23	7.94	<0.001
After grit removal	0.02	0.17	0.11	0.12	0.17	0.22	7.82	<0.001
Primary clarified wastewater	0.02	0.16	0.1	0.11	0.17	0.21	7.17	<0.001
Treated effluent	0.02	0.15	0.06	0.11	0.16	0.20	0.08	<0.001
Reject water	0.005	0.13	0.09	0.05	0.16	0.1	10.15	<0.001
Thickened primary sludge	0.02	0.46	1.8	0.41	0.57	0.75	58.5	<0.001
Thickened secondary sludge	0.02	0.67	2.71	0.63	0.7	1.03	355.8	<0.001

Table 2. The main technological parameters used to the calculation of HM balance
(The figures are average of the period studied)

Volume of wastewater			Thickened sludge streams	Sludge dewatering				
influent				primary	secondary	volume	dry solid content	
I. stream	II. stream	total	common				before	after
m ³	m ³	m ³	m ³	m ³	m ³	%	%	
7 250	6 500	13 750	13 190	112	134	243	2.39	23

Table 3. Daily HM mass in the streams shown in Fig. 1

Samples	Cd	Co	Mn	Ni	Cr	Cu	Fe
	g/d	g/d	g/d	g/d	g/d	g/d	g/d
Raw wastewater	150	1 100	800	800	1 200	1 500	51 600
After grip removal	149	1 080	682	778	1 132	1 448	50 826
Primary clarified wastewater	144	1 048	614	706	1 093	1 388	46 595
Treated effluent	139	991	400	697	1 049	1 310	516
Reject water	1.6	38.5	28	14.4	48	28.5	3 044
Thickened primary sludge	2.4	51.7	221	46.4	63.3	84	6 553
Thickened secondary sludge	1.5	42.9	170	52.8	78	82.5	44 170
Digested dewatered sludge	2.5	90.2	363	84.8	93.3	138	47 679

In the sewage entering the plant the concentration of the different HMs has not changed considerably. As a result of that their mass stream had to change according the volumetric load of the plant. This was not true for the sludge streams, as the plant had a great equalization for the total sludge mass.

From Tables 1-3 it can be seen that concentrations of the different heavy metals measured had no significant change or decrease in the sewage streams and even in the treated effluent. At the same time the sludge containing streams, with around 1 and 3-4 percentage of dry material contained much more HMs. HMs removed from the influent (dissolved and solid) were expected to concentrate in the sludge phase of this streams and the dewatered sludge as well. This means that removal of HMs in this treatment facility was very poor. We could not find any reason for that, but the very low specific organic material load and the high sludge age may result in such an influence for the dissolution of the HMs to the liquid water phase.

From data of Table 1, the remaining HM content of the different streams measured was calculated. The results can be seen in Table 4 (order of metals as above). According to the measurement Cadmium was not removed from the sewage with the AS treatment. It was totally missing from the reject water of the plant and only 4% of the Cd load could be adsorbed on the final sludge produced. In comparison with Cd loading, the loads with Co, Mn, Ni and Cu were by one order of magnitude higher in a very narrow daily load range (800-1600 g/d). A considerable part of all these metals left the plant with the treated effluent. Not more than 4-5 % of the Co remained in the dewatered sludge according to our measurements and only 1-3 % of the total load was recycled to the inlet point with the reject water.

In spite of Cd and Co just a bit less than half of the Mn remained in the purified water and the rest was concentrated in the dewatered sludge. A 1.5% of the Mn content of this sludge was recycled to the inlet with

the centrifuge water. The metal adsorption of the primary and secondary sludge seemed very similar which is also proved with the fact that after primary clarification $\frac{3}{4}$ of the inlet Mn load remained in the sewage stream. In case of Ni only 15-20% of its load will remain in the solid residue and one tenth of that is recycled to the inlet with the reject water. The Ni seems to be adsorbed and built in to the two types of sludge in similar ratio. Chromium seems to be bounded to the primary sludge part while only a smaller portion was removed by the biology. These two stages however could not remove more than 5% of the influent load. This removal seems enough as the inlet concentration is low enough.

The removal efficiency of the treatment for Cu seemed better than the metals mentioned before but it was not more than 15-20%. Most of the removed Cu was captured in the secondary sludge. That is the reason why the high Cu concentrations of some municipal sewage sludge can be caused by the high Cu content of the raw sewage. According to our study the Fe is in the highest concentration in the sewage. Around 500 times higher than the metals mentioned before. After the total treatment its concentration is very similar to that of the upper mentioned metals. The Iron is oxidized in the AS process and is built into the biomass as hydroxide. The removal efficiency was 99 % according to the measurements.

From Table 3 it can be seen that sand removal has practically no influence on the metal content of the sewage. In the primary clarifier the metal removal is also poor enough except for Mn and Fe. Removal of metals with the secondary sludge was just a bit more efficient then with the primary one. Only Mn and Cu were better adsorbed on the biomass. However Fe was almost totally removed with the sludge phase. In the whole treatment Mn removal was around 70 % and that of the iron was 99%. Concentration of the other metals tested had decreased with only 5-15%.

Depending on the sludge removal from the digesters to centrifuges the average daily reject water

quantity is around 200 m³. With this flow only 2-3% of the HM load is recycled to the sewage stream entering the plant. This is such a minor ratio of the HMs that separate metal removal from that stream can not have reality. The biggest problem of this sewage treatment facility however is the very poor removal of the HMs with the sludge produced which means a similar average removal of these pollutants from the sewage as well. This can properly be seen from Table 1 from the inflow and treated effluent concentrations and Table 4 showing the removal percentages of the metals in the processing steps.

From other studies we could learn that around half or a bit bigger portion of these metals can be removed with the sludge residue. In our examinations we could not measure such high removals neither in the primary nor in the secondary sludge. Moreover to that, only a small ratio of the metal content of the raw sludge can dissolve during the anaerobic digestion. According to our measurements most of the HMs left the plant with the clarified effluent. Changes of the total heavy metal content of the different streams in the plant tested are summarized in Fig. 2.

The streams of the Figure show the average daily quantities in percentages of the inflow (100 %). These data are well representing the removal of the metals tested except the removal of iron. Fe is very efficiently removed with the different sludge fractions and it practically cannot dissolve even in the digester, as the hydroxides and sulphides of the iron are very strongly stacking to the bioproduct of the treatment. The figure clearly proves that HM's recycle with the reject water is a very small ratio of their load. The dewatered digested sludge removed also very small ratio of the sewage load. Several publications mention effective (over 80-90%) heavy metal adsorption in activated sludge.

During our experiment we experienced inverse of this. Increased metal adsorption could be caused by the high metal concentration in liquid phase. This is typical of industrial wastewater such as electroplating sewage. The metal content in communal wastewater is far less than in some industrial wastewater streams.

There were no researchers who investigated the change of heavy metal concentration in each purification stage at municipal wastewater treatment plant. So there weren't any study for metal concentration of biological purified wastewater. On the contrary, there are some publications in which heavy metal content of sewage sludge is submitted.

In dewatered communal sludge heavy metals could be present in concentration over limit value. Because of this there is a significant regard for the metal content of sludge. If heavy metal limits would be less strict the metal concentration of sewage sludge wouldn't generate problem. Irrespectively of heavy metal problem it must be mentioned that the soil requires some micro nutrient such as copper and zinc. These components of all metals often cause problem in communal sewage sludge. As municipal wastewater doesn't contain heavy metals over limit value, the purified water can't contain them in problematic concentration. Components present in concentration under limit value don't get great attention. However the average metal concentration of communal wastewater generates higher metal content in produced sludge. Metal content in sludge depends on the adsorption capacity of activated sludge and the metal forms, among others.

For example in electroplating sludge there are surely more heavy metals but it wasn't measured in researches. At the same time if these wastewater streams would be treated by biological methods, the purified wastewater could contain toxic metals in higher concentration.

4. Conclusions

The present study demonstrates that in a municipal sewage treatment plant in an activated sludge POTW the removal of heavy metals can be very moderate and far from the removal percentages published in several studies.

Biggest part of the HM content of the inlet sewage remains in the liquid phase and quits the system with the treated effluent. Far not half, but only a minor ratio is adsorbed or accumulated in the biomass produced in the treatment.

The primary and secondary sludge had around similar HM removal, except for copper which is mainly removed by the secondary sludge. HM content of the mixed primary and secondary sludge decreased to a small extent during digestion. The reject water containing the dissolved metals had so low metal concentrations that its separate treatment does not seem favourable. It contains only 2-3 % of the total HM load of the plant. At the same time 85-95 % of that is leaving the plant with the treated effluent.

Table 4. Relative quantity of the different HMs in the streams measured as percentage of the influent concentrations

<i>Samples</i>	<i>Cd</i>	<i>Co</i>	<i>Mn</i>	<i>Ni</i>	<i>Cr</i>	<i>Cu</i>	<i>Fe</i>
	%	%	%	%	%	%	%
Raw wastewater	100	100	100	100	100	100	100
After grip removal	99	98.1	85.2	97.2	94.3	96.5	98.5
Primary clarified wastewater	96.2	95.2	76.7	88.3	91.1	92.5	90.3
Treated effluent	92.5	90.1	50	87.1	87.4	87.3	1
Reject water	1.3	3.5	3.5	1.8	4	1.9	5.9
Thickened primary sludge	1.6	4.7	37.6	5.8	5.3	5.6	12.7
Thickened secondary digested and dewatered sludge	1	3.9	31.3	6.6	6.5	5.5	85.6

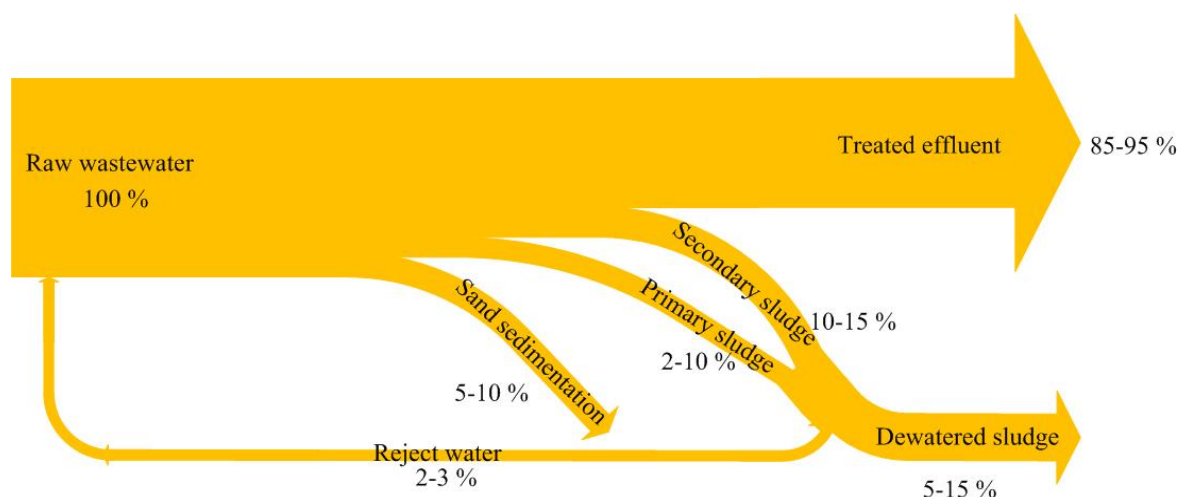


Fig. 2. Removal of the heavy metals in the AS POTW

Consequently we could not find extremely high HM concentration in the dewatered digested sludge of this plant. Contrarily because of their high solubility in water, heavy metals can be absorbed by living microorganisms.

The sludge reprocessing and reuse has no problem in the plant. The low influent concentrations of the HMs at the same time may be originated from the merely pure municipal effluent from the small town and its surrounding villages.

Acknowledgements

Financing the research was provided by Baross Gábor Project of 2009-2010 under the name of the subproject „Infrastructure of Research Development - KD_INFRA_09-SZVISZAP” (Qualification of the sewage sludge of the Hungarian POTWs – for possible decrease of their HM content). The foundation of the project was insured by the Hungarian National Research and Technology Office (National Innovation Office). The project has been realized thanks to the Research and Technology Innovation Fund.

References

- Álvarez E.A., Mochón M.C., Sánchez J.C.J., Rodríguez M.T., (2002), Heavy metal extractable forms in sludge from wastewater treatment plants, *Chemosphere*, **47**, 765-775.
- Barakat, M.A., (2011), New trends in removing heavy metals from industrial wastewater, *Arabian Journal of Chemistry*, **4**, 361-377.
- Gulyás G., Pitás V., Kárpáti Á., (2013), Measuring the heavy metal concentrations of digested dewatered sewage sludge with the help of microwave digestion (in Hungarian), *Maszesz Hírcsatorna*, **3-4**, 3-11.
- Karvelas A., Katsoyiannis A., Samara C., (2003), Occurrence and fate of heavy metals in the wastewater treatment process, *Chemosphere*, **53**, 1201-1210.

- Lester J.N., (1983), Significance and behaviour of heavy metals in wastewater treatment processes. I. Sewage treatment and effluent discharge, *Science of the Total Environment*, **30**, 1-4.
- Liu T., Yang X., Wang Z.L., Yan X., (2013), Enhanced chitosan beads-supported FeO nanoparticles for removal of heavy metals from electroplating wastewater in permeable reactive barriers, *Water Research*, **47**, 6691-6700.
- Martín-Lara M.A., Blázquez G., Trujillo M.C., Pérez A., Calero M., (2014), New treatment of real electroplating wastewater containing heavy metal ions by adsorption onto olive stone, *Journal of Cleaner Production*, **81**, 120-129.
- Moussa H., Qdais H.A., (2004), Removal of heavy metals from wastewater by membrane processes: a comparative study, *Desalination*, **164**, 105-110.
- Özbelge T.A., Özbelge H.Ö., Tursun M., (2005), Effects of hydraulic residence time on metal uptake by activated sludge, *Chemical Engineering and Processing*, **44**, 23-32.
- Sörme L., Lagerkvist R., (2002), Sources of heavy metals in urban wastewater in Stockholm, *The Science of the Total Environment*, **298**, 131-145.
- Stephenson T., Jester J.N., (1987), Heavy metal behaviour during the activated sludge process – I. Extent of soluble and insoluble metal removal, *Science of the Total Environment*, **63**, 199-214.
- Wang C., Li X.-C., Ma H.-T., Qian J., Zhai J.-B., (2006), Distribution of extractable fractions of heavy metals in sludge during the wastewater treatment process, *Journal of Hazardous Materials*, **A137**, 1277-1283.
- Yan X., Li Q., Chai L., Yang B., Wang Q., (2014), Formation of abiological granular sludge – A facile and bioinspired proposal for improving sludge settling performance during heavy metal wastewater treatment, *Chemosphere*, **113**, 36-41.