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Contribution to the study of selected heavy metals in urban wastewaters using ICP-MS method

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Abstract. Heavy metals pose a significant risk to all environmental elements and human health. The danger lies in the fact that they can be toxic even at low concentrations. For this reason, inductively coupled plasma mass spectrometry (ICP-MS) was chosen from all available methods to monitor the concentration of selected heavy metals. In comparison with other methods, very low concentrations of monitored substances (in µg /l) can be determined by ICP-MS.

This paper deals with the monitoring of the concentration of selected heavy metals at the inlet and outlet of the municipal wastewater treatment plant, namely lead, cadmium and nickel. The results show that the purification process has a positive effect on the reduction of the concentration of heavy metals in wastewater.

1. Introduction

According to one definition, heavy metals can be defined as metals whose specific gravity is greater than 5 g.cm⁻³. These substances have many negative properties, including long half-life, high storage capacity and persistence. Because to these properties, heavy metals pose a danger to all environmental elements and thus to human health. Diseases of the human nervous and immune systems are often associated with heavy metals. This research deals with three toxic heavy metals - lead, nickel and cadmium in urban wastewaters. The area of the Ostrava region from which the analyzed wastewater samples originate is marked by industrial activity. This is one of the main sources of toxic metal pollution in environment [1, 2].

Heavy metals in the environment are mainly related to anthropogenic activity. The main source of heavy metals in the aquatic environment is wastewater originating mainly from industrial and agricultural activities. Also, an important source is atmospheric precipitation polluted by the fumes generated by the combustion of fossil fuels. Trace amounts of heavy metals occur naturally in waters. The problem arises when the concentration of these substances in water is higher. Heavy metals negatively affect the aquatic environment even at low concentrations [2, 3, 4].

The concentration of heavy metals in wastewater is also dealt with in European legislation. Specifically, Directive 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy. In accordance with European Union law, the Government Decree no. 401/2015 Coll is effective in the Czech Republic since 2016. This regulation includes environmental quality standards (EQS) that express the concentration of a substance or group of substances in water, aquatic sediments or aquatic living organisms, the exceeding of which could pose a risk to human health and the environment. Two forms are distinguished - EQS-AA, which is an environmental quality standard expressed as an annual average value, and EQS-MAC, where the environmental quality standard is expressed as a maximum allowable concentration and is not exceeded.

In this paper, the measured values were compared with the EQS-MAC limit values. The limit values of the monitored heavy metals according to the EQS-MAC are given in Table 1. According to the detected concentrations of Cd, wastewater is divided into five classes [5, 6].

In the human body, lead accumulates primarily in the bones. Here it negatively affects hematopoiesis, which may result in anemia. Lead ions are carcinogenic. This metal is also considered a neurotoxin. In addition to the nervous system, it also affects kidney and liver function. Its effects are dangerous for pregnant women as some lead compounds can penetrate the placenta and seriously damage the fetus.



The concentration of lead in wastewater was high especially in the past, when lead was a part of fuel. Today, it is mainly found in wastewater from metallurgy and ore processing [3, 4, 7].

Table 1. Permitted concentrations of selected heavy metals for individual classes according to EQS-MAC [6].

Heavy metal	Class	EQS-MAC [$\mu\text{g/l}$]
Cd	I	≤ 0.45
	II	0.45
	III	0.6
	IV	0.9
	V	1.5
Pb		14
Ni		34

Cadmium ranks among highly toxic metals. It is especially dangerous for humans to inhale cadmium-containing dust and fumes. Mutagenic, teratogenic effects have been confirmed with this metal and it also may cause chromosomal abnormalities. In human body, cadmium accumulates in the kidneys. Due to this metal, the kidney, liver, lung and reproductive organs are most often damaged. Cadmium enters the wastewater and atmosphere mainly through the treatment of lead and zinc ores containing this metal. Other sources include phosphate fertilizers, sewage sludge and wastewater from galvanizing process and production of nickel-cadmium batteries. The presence of cadmium in waters is always accompanied by a low concentration of zinc [2, 3, 7].

Nickel is a potential carcinogen. Some of its salts are toxic, such as sulfates, chlorides, phosphates and nitrates. The most common consequences for human health are lung cancer, which is a consequence of the inhalation of nickel-containing dust. Nickel in high concentrations can cause damage to the heart muscle, central nervous system and kidneys. Dermatitis is a common problem associated with this metal. Nickel negatively affects all environmental elements. The most common anthropogenic sources are metallurgical plants, especially wastewater from metal surface treatment and municipal waste incineration plants [3, 4].

Due to the ability to detect low concentrations of substances occurring in wastewater, inductively coupled plasma mass spectrometry was chosen from the available methods. This method can be used to obtain results within $\mu\text{g/l}$ units.

2. Materials and Methods

Two samples of water were selected as the input water for this experiment, the water flowing into the municipal wastewater treatment plant and the purified wastewater from the same treatment plant. The concept of treatment at the selected wastewater treatment plant is based on mechanical-biological treatment of sewage and industrial water on the principle of low-load activation with nitrification and upstream denitrification with an automated control system for all technological processes. Anaerobically stabilized sludge is dewatered on centrifuges and hygienized with lime [8]. Each sample was subjected to a basic chemical analysis. Chemical oxygen demand was determined using potassium dichromate - method in tubes according to ČSN ISO 15705. Concentration of suspended solids was determined according to standard ČSN EN 872 and dissolved substances according to ČSN 75 7346. Both samples were then appropriately pretreated and analyzed by AAS and ICP-MS. The results obtained show that the AAS method is not suitable for these samples because the measured results are below the detection limit. For this reason, we continued to measure these samples using the ICP-MS method.

The ICP-MS method is one of the most used methods of inorganic mass spectrometry. This is an extremely sensitive method that allows for multi-element analysis. Among the advantages of this method is the possibility to determine a large number of metals and non-metals. One of the basic parts of this method is the ion source. The analyte molecules are ionized by the ion source. The resulting ions are then fed to a mass analyzer, in this case a quadrupole mass filter. This analyzer is made up of four

metal bars between which an ion stream is guided. It acts as a filter that selects individual ions according to their mass / charge ratio (m/z). The detector uses oscillating electric fields to make the individual ions begin to oscillate. However, oscillation is stable only for ions of a certain m/z ratio. These ions pass the analyzer further to the detector, which detects them. The other ions are carried out of the electric field and trapped on the quadrupole poles. Obtained data are evaluated by PC [9, 10].

Prior to ICP-MS analysis, samples were treated with nitric acid digestion according to ČSN EN ISO 15587-2 (757310). To 50 ml of each sample was added 5 ml of nitric acid p.p. purity. The resulting mixture was boiled. The boiling was maintained until the volume of the samples had dropped to 25 ml, i. e. in half. The samples were further filtered through medium-speed filter paper and filled up to 50 ml with distilled water.

After pre-treatment, samples were analyzed by AAS and ICP-MS. The analyzes AAS were performed on an Agilent 240 AA and ICP-MS analyses on an Analytik Jena PlasmaQuant MS Elite instrument. Each sample was analyzed a total of 3 times to minimize measurement error.

3. Result and Discussion

Prior to the analysis, the basic physicochemical properties were analyzed for each wastewater sample. The obtained results are shown in Table 2.

Table 2. Results of physicochemical properties of samples.

	Inlet	Outlet
pH [-]	7.61	8.06
Conductivity [$\mu\text{S}/\text{cm}$]	1300	1255
COD [mg/l]	349.11	27.58
Solutes [g/l]	0.322	0.488
Suspended solids [g/l]	0.055	0.008

The samples were then stabilized with nitric acid and analyzed by AAS and ICP-MS. The results are summarized in Tables 3 and 4. Each sample was analyzed a total of 3 times. The obtained values did not deviate too much from each other, therefore the average value was calculated from the obtained values, which was then compared with the EQS-MAC.

Table 3. Inlet results obtained by AAS and ICP-MS.

	AAS			ICP-MS		
	Pb [$\mu\text{g}/\text{l}$]	Ni [$\mu\text{g}/\text{l}$]	Cd [$\mu\text{g}/\text{l}$]	Pb [$\mu\text{g}/\text{l}$]	Ni [$\mu\text{g}/\text{l}$]	Cd [$\mu\text{g}/\text{l}$]
1	< 10	< 10	< 5	2.299	2.815	0.506
2	< 10	< 10	< 5	2.303	2.804	0.499
3	< 10	< 10	< 5	2.297	2.795	0.492
average value	-	-	-	2.300	2.805	0.499

The obtained results show that the inlet, while comparing indicator Cd with the EQS-MAC, belongs to Class 2. The measured value of the concentrations of the other two metals (Pb, Ni) is lower than the set limit values for EQS-MAC.

Table 4. Outlet results obtained by AAS and ICP-MS.

	AAS			ICP-MS		
	Pb [$\mu\text{g/l}$]	Ni [$\mu\text{g/l}$]	Cd [$\mu\text{g/l}$]	Pb [$\mu\text{g/l}$]	Ni [$\mu\text{g/l}$]	Cd [$\mu\text{g/l}$]
1	< 10	< 10	< 5	0.512	0.396	0.398
2	< 10	< 10	< 5	0.495	0.402	0.405
3	< 10	< 10	< 5	0.483	0.388	0.407
average value	-	-	-	0.497	0.395	0.403

The results obtained by ICP-MS analysis for the effluent from the wastewater treatment plant indicate that this sample meets the EQS-MAC in all monitored parameters. Based on the measured Cd value, this sample belongs to Class 1 on a five-step scale. Obtained values for Pb and Ni concentrations are significantly lower than the limit value determined by the EQS-MAC for these metals.

4. Conclusion

The concentrations of the monitored heavy metals were low in both samples, i.e. in the inlet and outlet from the municipal wastewater treatment plant. Higher concentrations were measured in the inlet wastewater, namely 2.30 $\mu\text{g/l}$ for Pb, 2.81 $\mu\text{g/l}$ for Ni and 0.50 $\mu\text{g/l}$ for Cd. In the treated wastewater, the detected concentrations were lower, Pb 0.50 $\mu\text{g/l}$, Ni 0.40 $\mu\text{g/l}$ and Cd 0.40 $\mu\text{g/l}$. As can be seen from the presented results, it is better to use ICP-MS analysis for these samples, due to the fact that the AAS method is not able to detect such low concentrations. Results clearly show that the purification technology has a positive effect on the reduction of the concentration of selected heavy metals in water. On the other hand, it must be taken into account that they accumulate in sewage sludge.

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