Cadmium in Industrial Wastewater

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Abstract

The concentration of cadmium in the industrial wastewater discharged from the aluminium and copper metal processing industry was analysed. The samples of water and sediment were taken from the Dragića Stream and the river Đetinja, downstream from the place where the wastewater from the metalworking industry flows into the Dragića Stream. According to the measured metal concentrations in the water and pursuant to the Regulations on Hazardous Substances in Water, issued by the Republic of Serbia, the water from the Dragića Stream belongs to the II class. Based on the obtained results, it was determined that the amount of metals in the water samples taken during the spring/summer season was relatively low, and that cadmium was dominantly present in the sediment.

Introduction

Cadmium is present in the atmosphere, soil and water, and its increased concentrations can cause serious damage to all living organisms [1]. Although has no essential biological function, its presence has been detected in more than 1,000 species of terrestrial and aquatic flora and fauna [2]. The concentration of cadmium in wastewater is usually low, but since it is a very toxic element, known for its tendency to accumulate in living organisms, it is important to determine even these minimum concentrations. Phosphatic fertilizers are the greatest anthropogenic source of cadmium in Western countries responsible for 58% of the total amount. Atmospheric gasses and sewage sludge contributes with cadmium release of 39 - 41% and 2 - 5%, respectively. The livestock manure contains 0.3 - 1.8 mg/kg Cd in its dry matter [3]. Cadmium is a relatively mobile element in the nature and the Cd^{2+} cation is stable at a wide range of pH values. It has a tendency to accompany zinc in the geological material, where the Cd/Zn ratio can range from 1/100 to1/1000. It is highly toxic for both humans and animals. It tends to accumulate in the organism, most often in kidneys, liver, pancreas, thyroid gland and bones. Cadmium displaces calcium in bones making them brittle. It has been proved to be cancerogenic and mutagenic [4].

Materials and methods

Eight different sampling localities were selected. The samples were taken from the Dragića Stream to which the wastewater from the metalworking industry is discharged, and downstream the river Đetinja, starting from the place where the Dragića stream joins it. Localities 1 - 4 are on the Dragića Stream, at each 50 meters, starting from the place where the wastewater reaches it. Location 5 is at the place where the Dragića Stream joins the river Đetinja, whereas localities 6 - 8 are downstream the river Đetinja, at each 500 meters. There is arable land at the distance of only a few meters from the bank (localities 6 and 7). Near locality 8, on the right side of the river, is an asphalted local road and, on the left side, there are meadows and agricultural land. At the place where the wastewater is discharged into the Dragića Stream, the water is grey, greasy and smelly. There is a lot of solid waste on the banks, as well as in the water itself (plastic bags, packages, glass, metal and textile products, rotten agricultural products) [5].

Preparation of water samples. The handling, storage and preparation of water samples were performed in compliance with the standard EPA 200.7 method [6]. Water samples were placed in plastic containers of 1L, previously washed with the 10% nitric acid solution. Immediately before the sample collection process, the containers were rinsed twice with the water from a certain locality and stored at the temperature of –30 ^{o}C until the beginning of the analysis.

Preparation of sediment samples. The surface sediment samples were collected into plastic containers of 1L, using the EPA 3050 B method [7]. Collected sample weighed 1-2 g (wet weight) or 1 g (dry weight) and 10 cm^3 of 1:1 nitric acid (HNO_3) was added to it. The sample was heated without boiling at the temperature of 95^{o}C for 10-15 minutes. After the colling, 5 cm^3 of cc HNO_3 was added to the sample. The same process was being repeated during the period of 30 minutes. The appearance of the brown fume indicated the oxidation of HNO_3. Then again 5 cm^3 of cc HNO_3 was added, until the reaction of the sample with HNO_3 at the temperature of 95^{o}C during the period of 2 hours was complete. The sample was cooled for 5 minutes. 2 cm^3 of water and 30 cm^3 of hydrogen peroxide (H_2O_2) were added to it. After heating at the temperature of 95^{o}C for 2 hours, the volume reduced to 5 cm^3. The purpose of this step was to ensure minimal losses because of the extremely strong reaction. 10 cm^3 of cc HCI was added, and the sample was kept for 15 minutes at the temperature of 95^{o}C, after which it was ready for the analysis.

Sampling methods. The inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the cadmium concentration in the solution. The ICAP 6500 Duo (Therm Scientific, USA) instrument was used, with the detection limit of 0.09 ppb.

Results and discussion

The quantity and quality of industrial wastewater can vary widely during a day, even when it comes from the same industrial plant. This is due to the dynamics of wastewater generation during the production process, but also due to the different intensity of operations in an industrial plant. Neither the quality, nor the contamination of wastewater, and therefore the total pollution caused by wastewater, is uniform, especially in the case of discontinual, batch production processes. In the metal processing industry, such as copper and alluminium mills, the quantity of wastewater is relatively small, but it contains very large and specific amounts of toxicants (extreme pH values, the presence of oil, heavy metals, copper, chome, lead, zinc and cadmium, as well as phenol). This can cause the changes in the physical and chemical conditions of the sediment containing such metals, which leads to the resuspension and dissolution of the contaminants adsorbed or coprecipitated in the sediment. The resuspension of a part of the sediment causes the increase in the concentration of heavy metals in the aqueous phase, no matter if these metals are in the suspended, collodal or dissolved form.

The cadmium concentrations in the wastewater and sediment samples collected on the Dragića Stream in the spring/summer 2009 (sample localities 1-8) are given in Table 1.

Table 1. Cadmium concentrations in water and sediment

Concentration of cadmium (mg/L)				
Sampling locality	Water		Sediment	
	spring	summer	spring	summer
1	0.0005	-	0.09	1.60
2	0.0005	0.0001	0.08	1.46
3	0.0009	0.0001	0.32	1.60
4	0.0030	-	0.43	1.02
5	0.0008	0.0001	0.15	1.46
6	0.0005	0.0001	0.65	0.007
7	0.0004	0.0001	0.14	0.02
8	0.0003	0.0001	0.24	0.01

The cadmium concentration in the water ranged from $1 \cdot 10^{-7}$ mg/L to 0.003 mg/L, and at all sampling localities, it was higher in the spring than in the summer, but did not exceed the maximum allowed concentration (MAC) [8]. The cadmium concentration in the sediment at the first five localities was higher in the summer, ranging from 0.007 mg/kg to 1.6 mg/kg, but not exceeding the MAC [9].

Based on the obtained results regarding the concentrations of metals in the water and sediment, it can be concluded that metal was dominantly present in the sediment. The water flow in the summer was substantially lower than in the spring. The Dragića Steram is directly affected by the industrial wastewater, with a low self-purification potential, which contributes to its poor quality. In the river Đetinja, the exacerbated quality of the sediment was detected. High cadmium concentrations in the samples collected in the summer were probably the result of the pressure coming from diffusion sources, such as the use of phosphate fertilizers in the agriculture, which were made from low quality raw materials. Serbia is known for the production of fertilizers by mixing raw materials and the sulfuric acid. And if there are any harmful admixtures in the raw materials (cadmium, uranium compounds, etc), these will end up in the final product [5].

Conclusion

The study included examination of industrial wastewater and sediments quality in terms of determination of cadmium concentration in Dragića Stream during the spring/summer 2009. According to the results, the sediment quality was significantly impaired due to the increased cadmium concentration, although it did not exceed the maximum allowed concentration. This leads to the conclusion that the metal concentration in the water was relatively low, compared with the sediment. Analysing these two media separately, cadmium concentration in the spring was higher in the water than in the sediment, at all sampling localities. This was due to the high flow of water in this period of the year, which prevented the precipitation of the analysed metal in the sediment.

The efficient implementation of certain technical and technological measures during the production processes in the metal processing industry could reduce the emission of cadmium and other heavy metals and ensure the protection of the environment from the pollution with heavy metals. Continual monitoring of the mobility of metals in the water/sediment system, together with the obtained result, could make possible to predict the measures necessary for the revitalization of the watercourses of the river Đetinja and Dragića Stream, since the presence of certain metals in the water and sediment has been proved.

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