THE CONTENTS OF COPPER AND ZINC IN THE WASTEWATER/SEDIMENT FROM THE METALWORKING INDUSTRY

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ABSTRACT

The wastewater and sediment from the Metalworking Industry Sevojno, Western Serbia, were analyzed. The samples of water and sediment were taken from the Dragića Spring and the River Djetinja, downstream from the place where the wastewater flows into the Dragića Spring. According to the measured concentrations of metals in the water and the Serbian Regulations on Hazardous Substances in Water the Dragića Spring belongs to the II class of water. 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, whereas their concentrations in sediment were dominant. By the linear correlation and regression analyses of the measured concentrations of heavy metals in water/sediment the quantitative dependence of the variables was determined. The MATLAB programme package was used to determine the polynomial model representing the distribution of the analyzed metals with increasing distance from the discharging place into the Dragića Spring. The status of the analyzed sediment/water system during the spring/summer 2009 indicated the limited process of adsorption.

Keywords: heavy metals, water, sediment, industrial wastewater, linear regression analysis

1. Introduction

Industrial wastewater represents the most important anthropogenic source of metals in the aquatic ecosystem. The distribution and migration of metals in aquatic ecosystems are determined by the character of sediments, as well as by the physical and chemical properties of metals. Metal concentration levels depend on pollution sources and the state of the production system, whereas they can range from traces to high concentrations (Aksentijević, 2011). Another important factor which influences the mobility of heavy metals is the concentration of organic matter in sediment, because of its high cation exchange capacity, as well as its large specific surface areas, often negatively charged. Due to the sediment represents an adsorption surface area, heavy metal can be easily retained from a solution and the increasing amount of organic matter in sediment generally causes the increase of metal mobility and the adsorption (Bergsten and Likos, 2006).

In an aquatic system, copper appears in three basic forms: suspended, colloidal and soluble. The amount of copper bounded to solid phase can range from 12-97% (Karbassi and Pazoki, 2015). High concentrations of copper in sediment are caused by its intensive adsorption. The adsorption rate depends on the presence of clay particles, ligands, humic and fulvic acids, iron and manganese oxides, pH values and the presence of other cations (Čolić and Petković, 2009). At low concentrations, copper is essential to most organisms, whereas at higher concentrations, it can be toxic.

In an aqueous solution, Zn^{2+} ion behaves as a highly acidic metal. It hydrolyses at pH 7 to 7.5, producing a relatively stable $Zn(OH)_2$. In water, it can occur as $ZnOH^+$ or Zn^{2+} ions. The amount of zinc in sediment mostly depends on the pH value and redox potential (Aksentijević, 2011). Zinc is an essential element and, in low concentrations it is necessary for living organisms, while it is toxic in higher concentrations (Salguiero *et al*. 2000).

The aim of the research was to determine the concentrations of copper and zinc in the spring/summer season 2009. from the wastewater/sediment of Metalworking Industry Sevojno. The results should enable validation of a mathematical model in terms of predicting the behavior of a substance in the given medium.

2. Material and methods

The town of Sevojno is in Western Serba, in the valley of the River Djetinja. Eight localities were selected (Figure 1, Aksentijević, 2011).

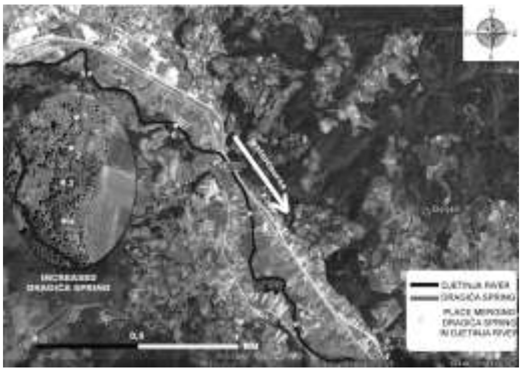


Figure 1: Sampling localities (Aksentijevic, 2011).

The samples were taken from the Dragića Spring, starting from the place of flowing Dragića Spring in the River Djetinja. Localities 1-4 are at each 50 m starting from the place of the wastewater discharging. Location 5 is at the point of pouring the Dragića Spring into the Djetinja River, whereas localities 6-8 are downstream the River Djetinja, at each 500 m. The discharged wastewater 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).

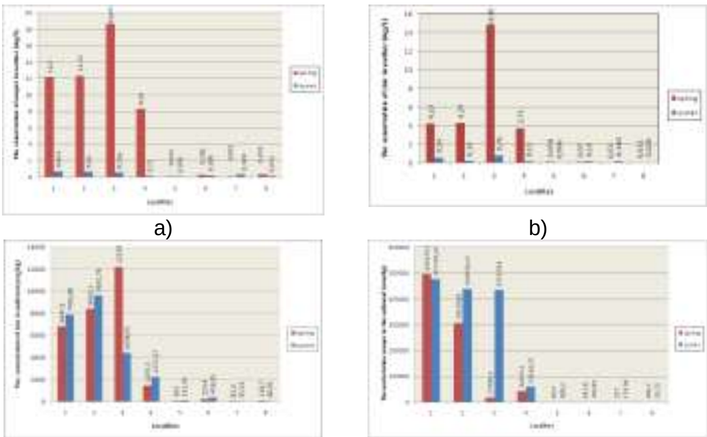
The water sample preparation was performed in compliance with the standard EPA 200.7 method (Spence and Cassap, 2008). The surface sediment samples were taken using the EPA 3050 B method (Erdogan, 2009). In order to determine the concentration of metals in a water/sediment, the inductively coupled plasma atomic emission spectrometry (ICAP 6500 Duo, USA) was used.

The general form of the regression model is presented as the regression function, f, between two variables: y = f(x). The Pearson coefficient, r, is used as a measure of the strength in a simple correlation analysis. Its values can range from -1 to +1 (Erić - Marinović, *et al*., 2001). In the case of adsorption on a solid surface the Freundlich isotherm model is mostly used: $C_s = K_f \bullet C_w^{1/n}$, where: C_s is the metal concentration in sediment (mg/kg); C_w is the metal concentration in water (µg/L); K_f is the capacity factor (mol/kg or mol/L), and n is the Freundlich exponent (Igwe and Abija, 2007). If the adsorption is favourable, the value of the Freundlich exponent n should be between 1 and 10 (Rao and Bhole, 2001). Smaller value of 1/n implies stronger adsorbate/adsorbent interaction, whereas the greater K_f indicates higher adsorption intensity (Igwe and Abija, 2007).

3. Results and discussion

The amount of wastewater in Metalworking Industry is relatively small, but the concentration of toxicants is specific and high (extreme pH values, presence of oil, heavy metals, as well as phenol). Because of that, the physical and chemical conditions in the sediment can change causing the resuspension and dissolution of the pollutants adsorbed or co-precipitated in the sediment. The resuspension of sediment causes the increase of metal concentration in the aquatic phase.

The amount of copper in the water was found to be greater in the spring than in the summer, varying between 0.059 and 18.69 mg/L, especially at localities 1-4, Figure 2. At the first four localities, the copper concentrations exceeded the MAC (Maximal Allowed Concentration) of 0.1 mg/L (Official Gazette of the SRS 31/82, 1982), which was the consequence of the direct wastewater discharge into the Dragića Spring. The zinc amount in the water was greater in the spring at localities 1-5, whereas at localities 6-8 the concetration of zinc was higher in the summer. Zinc concentrations varied between 0.011 and 14.85 mg/L, Figure 2b. The measured amounts at the first four localities exceeded the MAC of 0.2 mg/L for the I/II class water and 1.0 mg/L for the III/IV class water (Official Gazette of the SRS 31/82, 1982) during both the spring and summer. Metal concentrations in sediment are shown in Figure 2c and d. Since the Republic of Serbia has no appropriate regulations for the assessment of sediment quality, the assessment is performed by means of the comparison with the MAC of hazardous substances in soil: copper- up to 100 mg/L and zinc – up to 300 mg/L (Official Gazette of the RS, no. 23/94, 1994). With the exception of localities 2-4, the amount of copper in the sediment was higher during the spring, varying between 40.9 and 496679.7 mg/L, Figure 2d. The measured amounts of copper exceeded the MAC at all localities, except at locality 5 in the spring and locality 8 in the summer. The amount of zinc in the sediment was higher in the summer, except at locality 3, where the concentration was higher in the spring. The concentrations of zinc varied between 45.14 and 12220 mg/L. At localities 1-6 and 8, the measured amounts exceeded the MAC during both the spring and summer (Figure 2c).



a) b) c) d)

Figure 2: Variation of metal concentrations: copper (a) and zinc (b) in water, and zinc (c) and copper (d) in sediment, spring/summer 2009

Based on the obtained results, it was determined that metals were dominantly present in the sediment. The increased concentrations of metals were expected given the fact that the wastewater was discharged into the Dragića Spring, which has lower water level in the summer as well as low self-cleaning potential. At the River Djetinja the aggravated quality of sediment was detected. The results of the linear regression analysis obtained for copper and zinc during the spring/summer season are presented in Figure 3.

High positive values of the Pearson coefficient for copper (r = 0.930 during the spring and r = 0.714 during the summer) and zinc (r = 0.957 during the spring and r = 0.653 during the summer) confirm that the regression equations complied with the experimental data. The higher concentrations of copper and zinc in water (independent variables) contribute to the higher concentrations in sediment (dependent variables), and the intensive adsorption. Based on the intercept of regression lines, Figure 3, the following values of the Freundlich constants, K_f and 1/n, during the spring/summer were obtained for zinc: 0.246/0.030 and 0.513/0.538, and copper: 46.993/85.627 and 0.671/0.985, respectively. The values of the coefficient are $1/n < 1$ for the water/sediment system indicating the limited adsorption. The limitations occur if there is a limited number of active sites on the adsorbent, because C_s cannot increase indefinitely with the increasing C_w. The polynomial dependence of the meta distribution in water/sediment on the distance was obtained using the MATLAB programme package (Table 1).

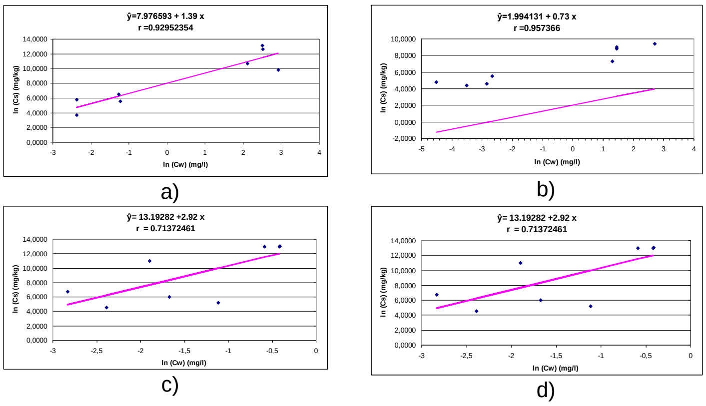


Figure 3: Correlation diagram of lnC_w (concentration of metals in water) and lnC_s (concentration of metals in sediment) for: a) copper - spring; b) zinc - spring; c) copper – summer; d) zinc – summer

Table 1: Distribution of metals in water/sediment during spring/summer based on distance

Distribution of metals based on distance	**Polynomial dependence**
zinc in water based on distance - spring	$y = 4.9822 \times 10^{-6} x^2 - 1.2155 \times 10^{-2} x + 6.5892$
zinc in sediment based on distance - spring	$y = 6.9384 \times 10^{-3} x^2 – 15.721 x + 7.5061 \times 10^3$
copper in water based on distance - spring	$y = 1.1355 \times 10^{-5} x^2 - 2.6208 \times 10^{-2} x + 13.0250$
copper in sediment based on distance - spring	$y = 3.1520 \times 10^{-1} x^2 - 6.5609 \times 10^2 x + 2.5152 \times 10^5$
zinc in water based on distance - summer	$y = 3.2529 \times 10^{-7} x^2 - 7.2665 \times 10^{-4} x + 0.3995$
zinc in sediment based on distance - summer	$y = 6.5342 \times 10^{-3} x^2 -14.4510 x + 6.5243 \times 10^3$
copper in water based on distance - summer	$y = 2.6029 \times 10^{-7} x^2 - 6.2479 \times 10^{-4} x + 0.4980$
copper in sediment - spring	$y = 0.3997 x^2 -8.7444 \times 10^2 x + 3.8023 \times 10$

4. Conclusion

The high degree of compatibility with the Freundlich model was determined by the regression and correlation analysis of the metal distribution between the solid and liquid phase. Using models, it is possible to observe a new relationship between the variables and use them to improve the efficiency of certain technologies in order to reduce the negative impact or improvement of the management of environmental quality. The obtained results are important for the revitalization of the watercourses of the River Djetinja and Dragića Spring, as they indicate the presence of certain metals in the water and sediment. The effective implementation of regulations, technical and technological measures and consistent monitoring of heavy metals provide a reduction in their concentration in the environment.

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