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Anna Hołda, Ewa Kisielowska*, Tomasz Niedoba**

CHEMICAL AND BIOLOGICAL ANALYSIS OF CHROMIUM WASTE

1. Introduction

Chromium is widely used in various industries, such as plating, tanning, paint and pigment production and metallurgy. It is well known that the toxicological and biological properties of this element depend on his chemical form. Two stable chromium species are known in the environment: Cr(III) and Cr(VI), and their toxicity is a function of the oxidation state and concentration of species. Cr(III) appears to be essential for mammals, whereas Cr(VI) has toxic and carcinogenic effects [5].

Chromium (VI) is an element harmful for environment and for human and is present as an air-, water-,and solid-pollutant. Because of the strong toxic properties and high mobility, wastes and sewers containing this element are being treated as dangerous [8, 11]. Even relatively small amounts of this element may be the source of danger for ecosystem because of the persistence of its compounds and possibility of multiplying its concentration [1, 6, 16].

Currently being applied chemical methods of waste containing chromium compounds treatment, as precipitation, reduction, ion exchange or filtration are not efficient when the metal concentration in wastes is small, are expensive and generate high amounts of wastes, which after placing in storage yard are always source of its slow and systematical degradation [9].

The economic and also friendly to environment alternative for chemical methods may be biotechnological [2] processes leading to limitation of chromium amounts introduced to environment by selective application of microorganisms: fungi [3, 4, 7, 13, 15] and bacteria [10, 12, 14, 17, 18].

The purpose of investigation presented in the paper is chemical and biological analysis of post-chromium mud.

* Wydział Górnictwa i Geoinżynierii, Akademia Górniczo-Hutnicza, Kraków

2. Methodology of research

2.1. Sampling and analysis of post-chromium mud

The samples of after chromium mud were collected from three various storage yard parts. The first sample was the material from the surface part of the storage yard. The second one was collected from the vertical slope created as a result of subsiding, on about 2 m depth from the storage yard top. The third one was obtained from the depth of 20 cm. All samples were transported in a fridge to laboratory and analyzed within 6 hours from the sampling time. The contents of chromium(VI) was determined in water extracts, done according to the norm PN-Z-15009 by the method of flow coulometry by means of apparatus EcaFlow 150GLP, applying calibration by method of model curve.

The determination of chromium by flow coulometry is based on utilization of inner electrode coulometric titration. The porous working electrode is being filled with sample solution and Cr(VI) is electrochemically reduced to Cr(III) and the load required to conducting this process is registered (1):

$$CrO_4^{2-} + 8H^+ \rightarrow Cr^{3+} + 4H_2O - 3e^- \quad (1)$$

2.2. Microbiological quantitative and qualitative analysis of samples

In purpose of microbiological analysis, the analytical samples of weight 10 g were taken from the post-chromium mud, which were transferred into Erlenmayer colbs, containing 90 ml of physiological liquid. Next, the samples were shaken during 15 minutes and after this time they were left for solid contents sedimentation. Such prepared solutions were diluted in range 1:10, from which further dilutions were made, 1:100 and 1:1000. In purpose of determination of mesophilous and psychrophilous bacteria, the inoculation was performed by the method of plated cast on MPA nourishment and such preparations were incubated, respectively for 72 h in room temperature and in 37°C during 24 h. To determine the microfungi, the inoculation was performed by method of abrasive plate on the Czapek-Dox base and the obtained preparations were incubated in temperature of 28°C during 72 h.

In purpose of bacteria observation, preparations were made coloured by simple method. In case of fungi, the preparations, made from the fungi fragments submerged in Lugol liquid and covered with micro cover glass, were observed in 400 times magnification.

3. Results

3.1. Chromium contents determination

The contents of chromium(VI) in individual analytic samples prepared with application of water extracts, was re-calculated on 1 kg of dry waste according to the formulae (2):

$$q = \left(V_0 \cdot c\right) / m \tag{2}$$

where:

V_0 — water volume added to leaching, l,
c — concentration of the researched component, mg/l,
m — mass of investigated dry sample, g.

The results were given in table 1.

The total concentration of chromium(VI) in samples of post-chromium mud and summary chromium contents re-calculated for 1 kg of dry waste were given in table 2.

TABLE 2
Total chromium(VI) concentration in samples of post-chromium mud

Number of sample	$c = \overline{c_I} + \overline{c_{II}} + \overline{c_{III}}$ mg/l	$Q = q_I + q_{II} + q_{III}$ g/kg
1	764.9	7.649
2	2111.2	21.112
3	1055.1	10.551

3.2. Microbiological qualitative and quantitative analysis of samples

The collected samples of post-chromium mud were microbiologically analyzed in purpose of selecting microorganisms resistant to influence of high chromium(VI) concentrations. In case of bacteria the number of grown colonies was re-calculated for 1g of wastes according to the formulae (3).

$$A = a \cdot b \tag{3}$$

where:

A — number if bacteria for 1g of wastes,
a — number of colonies,
b — level of dilution.

The results of qualitative and quantitative analyzes were shown in Tables 3 and 4.

TABLE 1

Chromium concentrations in individual samples

Number of sample	c_I, mg/l	$\overline{c}$	σ	q_I, g/kg	c_{II}, mg/l	$\overline{c}$	σ	q_{II}, g/kg	c_{III}, mg/l	$\overline{c}$	Σ	q_I, g/kg
1	426,8 418,8 412,6	419,4	0,36	4,194	183,0 186,3 187,3	185,6	0,23	1,856	150,2 160,5 169,0	159,9	0,94	1,599
2	1573,5 1615,5 1632,5	1607	0,60	16,07	286,8 288,6 289,0	288,2	0,06	1,882	213,1 217,2 217,5	216,0	0,25	2,160
3	676,0 658,8 643,4	659,4	0,81	6,594	212,1 219,98 223,8	218,6	0,59	2,186	176,5 177,7 177,1	177,1	0,06	1,771

TABLE 3

Number of bacteria and mesophilous fungi in individual samples and dilutions

Number of sample	Number of *Mesophilous* bacteria in dilutions			Number of *Psychrophilous* bacteria in dilutions			Number of *Fungi* colonies in dilutions	
	1:10	1:100	1:1000	1:10	1:100	1:1000	1:10	1:100
I	180	3	1	>500	201	2	0	4
II	0	0	0	0	0	0	60	31
III	14	2	1	>500	171	6	0	0

TABLE 4

Sorts of microorganisms occurring in researched samples

Number of sample	*Mesophilous bacteria*	*Psychrophilous bacteria*	*Fungi*
I	*Bacillus sp.* *Micrococcus sp.* *Diplococcus sp.*	*Bacillus sp.* *Bacterium sp.* *Micrococcus sp.* *Diplococcus sp.*	*Aspergillus sp.* *Trichoderma sp.* *Acremonium sp.*
II	–	–	*Penicillium sp.* *Rhizopus nigricans*
III	*Sarcina sp.* *Bacillus sp.*	*Bacillus sp.* *Diplococcus sp.* *Tetracoccus sp.*	–

4. Conclusions

— Concentration of chromium(VI) in wastes of post-chromium mud is dependent on the depth. The sewers, infiltrating through the storage yard massif, are washing the chromium(VI) out from surface and deeper layers, generating there high concentrations of this element ions.

— The concentration of chromium(VI) above 2000 mg/l is toxic for psychro- and mesophilous bacteria, stopping the growth of their colonies, what limits their application to remove high contents of this element from wastes.

— Fungi from sort Rhizopus sp. and Penicillium sp. are tolerant for high concentrations of chromium(VI). It may be used to remove this metal ions from the solution during the inner cellular bioaccumulation or biosorption process.

The application of mould to lower the chromium(VI) contents may be the alternative for chemical methods, which are expensive and generate high amounts of wastes.

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