

LEAD AND CHROMIUM SORPTION ONTO BASIC OXYGEN FURNACE SLAG

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<https://doi.org/10.37904/metal.2022.4382>

Abstract

Lead and chromium removal from water solutions using the basic oxygen furnace slag was investigated. Calcium, iron, and silica were the main components of the slag. The samples were characterized by means of the thermal, surface, and mineralogical analysis and infrared spectroscopy. The experiments were performed at the ambient temperature. Chromium adsorption proceeded according to the Langmuir isotherm and lead adsorption proceeded according to the Freundlich isotherm. The sorption capacity over 150 mg/g was reached for chromium and the value was higher than 250 mg/g for lead. Kinetic data were analysed using the pseudo-first, pseudo-second and intra-particle diffusion models. Adsorption data of chromium were correlated with the pseudo-second-order kinetic model and lead sorption was very quick and the models could not be applied.

Keywords: Chromium, lead, slag, adsorption

1. INTRODUCTION

Lead and chromium belong among the most toxic heavy metals contained in the wastewater [1]. Because of their high solubility, they tend to accumulate in the food chain and can be absorbed by living organisms [2]. Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals. Metallurgical wastes or fertilizers are also sources of heavy metals. Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. Adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals. Various low-cost adsorbents, derived from agricultural waste industrial by-product, natural material, or modified biopolymers have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater [3]. Chromium and lead sorption onto slag was studied e. g. in [4]. Simultaneous sorption of Ni, Cr, Cd and Pb ions using clay was investigated in [5]. The sorption capacities usually reach maximum 100 mg/g using untreated natural materials. The kinetic studies were carried in [6-9]. The aim of this study was to measure the sorption capacity of the basic oxygen furnace slag and the kinetics of the chromium and lead sorption.

2. EXPERIMENTAL

2.1. Materials and methods

The initial stock solution of Pb(II) and Cr(III) with the concentration of 1000 mg dm⁻³ was prepared by dissolving Pb(NO₃)₂ and Cr(NO₃)₃•9H₂O in deionized water. 50 dm⁻³ of the solutions of various concentrations were prepared by dilution in distilled water. The steel-making slag was ground using the epicyclic ball mill RETSCH and sieved. The fraction under 0.1 mm was used. 0.1 - 1g of the slag was put into the plastic bottles and treated for 0.5 - 48 hours. The leaching experiments were carried out at the ambient temperature (22±2°C) in a shaker at 180 rpm. After the filtration, the solutions were analysed using AAS. The crystalline phases of the slag were identified by the powder diffractometer MiniFlex600 with Co lamp 600 W, Theta / 2 Theta), Rigaku, Japan. The infrared (IR) spectra of some samples were measured on FT-IR spectrometer Nicolet iS50

(ThermoScientific, USA) with DTGS detector by potassium bromide pellets technique in spectral region 4000-400 cm^{-1} . The surface analysis was carried out using physisorption of nitrogen on Sorptomatic 1990, Thermo Finnigan, Italy. Thermal analysis was performed using TA Instruments Discovery SDT 650 with autosampler, heating rate 10°C/min, air, sample weight 20 mg.

2.2. Results and discussion

The chemical composition of the slag can be seen in **Table 1**. The mineralogical composition is shown in **Figure 1**.

Table 1 Chemical composition of the slag determined by AAS and XRF (wt %)

Ca	Mg	Fe	Mn	Al	Si	Zn	Cr	Pb	Cd
21.8	4.1	28.3	4.4	1.4	6.7	0.10	0.28	0.028	0.0014

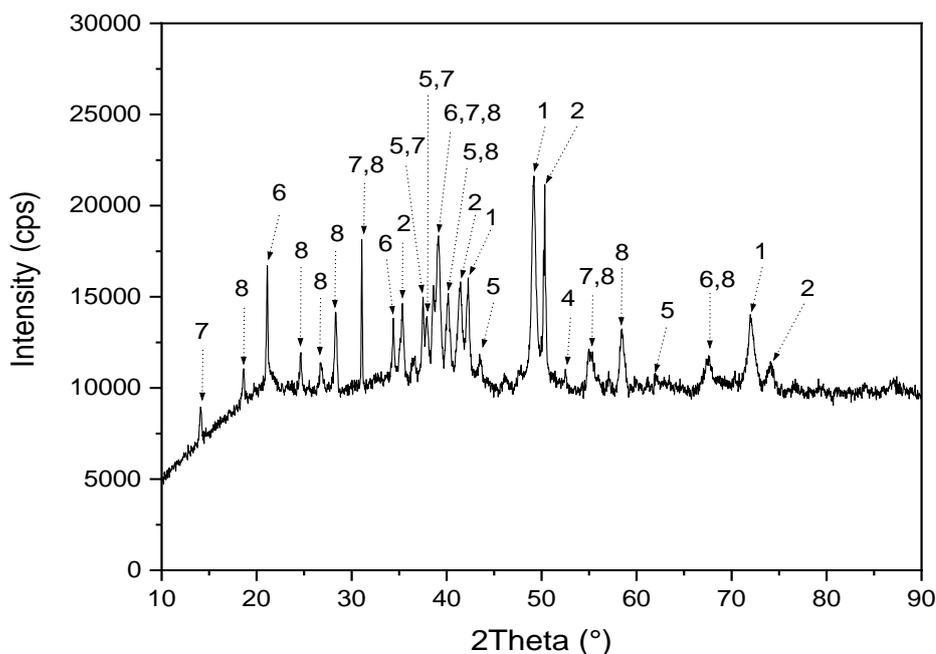


Figure 1 XRD patterns of the steel-making slag before sorption

1 - FeO (89-0686) Wustite, 2 - Fe₃O₄ (75-0449) Magnetite, 4 - MgO (85-5625) Periclase, 5 - Ca₂(SiO₄) (83-0464) Larnite, 6 - Ca₁₂Al₁₄O₃₃ (48-1882) Mayenite, 7 - Ca₂FeAlO₅ (72-7995) Brownmillerite, 8 - Ca(Fe 0.77Mg 0.22)(SiO₄) (87-2073) Kirschsteinite

The surface analysis of the slag showed that the specific surface is 6 m²/g, the mesopores volume 0.074 cm³/g and the micropores volume 0.003 cm³/g. The slag can be characterized as almost non-porous.

Figure 2 presents the results of the thermal analysis of the basic oxygen furnace slag. The first mass loss at 60-400°C is associated with the dehydration and dehydroxylation of various hydrates which need not be seen during the XRD analysis because of their amorphous character. The second mass loss starting at 640°C can be attributed to the decomposition of CaCO₃. It was not found during XRD analysis, but carbonates were identified during FTIR analysis. The last weight increase starting at 700°C can be probably attributed to the magnetite - hematite oxidation.

The results of the FTIR analysis can be seen in **Figure 3**. The most of spectral bands presented in IR spectra belong to O-H vibration of water. The spectral bands above $3,000\text{ cm}^{-1}$ belong to stretching vibration of O-H group of water. The weak and narrow bands above $3,600\text{ cm}^{-1}$ can be assigned to O-H stretching vibration of water in lattice of inorganic compounds (inorganic hydrates). The very broad and intensive band at $3,332\text{ cm}^{-1}$ in the sample *Cr* (and a weak but relative broad band at $3,437\text{ cm}^{-1}$ in the sample *Pb*) is assigned to stretching vibration of O-H of physical adsorbed water. Also, another bands can be assign to vibration of O-H of physical adsorbed water. The band of deformation (in-plane) O-H vibration of physical adsorbed water are presented at approx. $1,650\text{ cm}^{-1}$ (weak band at $1,664\text{ cm}^{-1}$ in the *Slag* sample; weak band at $1,658\text{ cm}^{-1}$ in the *Blank* sample; weak band at $1,634\text{ cm}^{-1}$ in the *Pb* sample; and broad band at $1,631\text{ cm}^{-1}$ in the *Cr* sample). The deformation (out-of-plane) O-H vibration of physical adsorbed water could be seen at approx. 500 cm^{-1} . In the samples *Slag*, *Blank*, and *Pb*, this band only makes deformation of spectral baselines in this region. The broad strong band of this vibration completely overlap above mentioned spectral region in the sample *Cr*. The band of this vibration is present in all spectra. The bands are clearly presented in samples *Slag*, *Blank*, and *Pb*; completely overlap by broad band of out-of-plane deformation vibration of physical adsorbed water are in sample *Cr*. The spectral bands at approx. $1,450\text{ cm}^{-1}$ (E'), 875 cm^{-1} (A_2''), and 715 cm^{-1} (E') are due to vibration of carbonates. The data in parentheses indicate the group of symmetry mentioned vibrations. All these bands are presented in the sample *Slag* and *Blank*; only two bands (at $1,417\text{ cm}^{-1}$ and at 876 cm^{-1}) are presented in the sample *Pb*; and only one band (at 1469 cm^{-1}) is presented in the sample *Cr*. A narrow band at $1,385\text{ cm}^{-1}$ (in the spectrum of sample *Pb*) belongs to stretching vibration of nitrates.

To verify the possibility to use this material for the heavy metals' removal, a blank experiment was carried out. 1g of the slag was leached with 50 mL of water for 24 h. The solution contained 208 mg/L of calcium, 0.37 mg/L of iron and less than 0.1 mg/L of cadmium, chromium, manganese, zinc, and lead. The pH value was 11.64. A great amount of calcium and small part of iron pass to the leach liquor from the adsorbent.

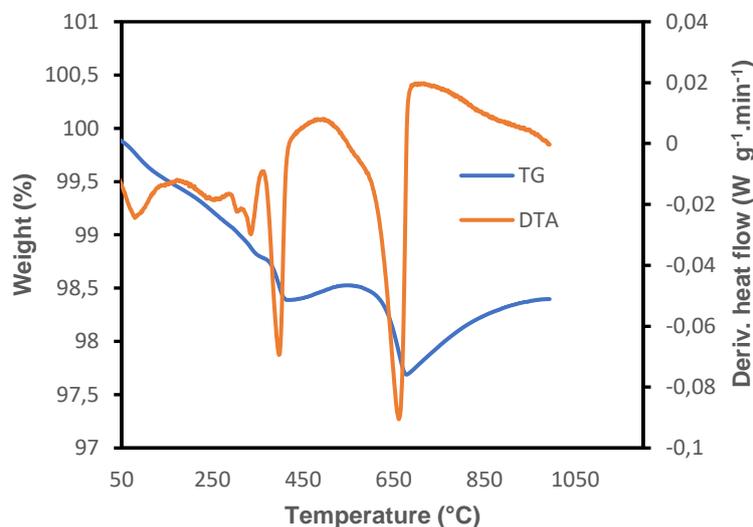


Figure 2 Thermal analysis of the original slag

Three kinetic models were tested -pseudo-first order (equation 1), pseudo-second order (equation 2) and intra-particle diffusion (equation 3).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{t}{q_e} \quad (2)$$

$$q_t = k_i t^{0.5} + C \quad (3)$$

K_1 is the rate constant for the pseudo-first-order model equation (min^{-1}), k_2 -the rate constant for pseudo-second-order kinetic model equation ($\text{g}/(\text{mg min})$), k_{id} is the rate constant of the intra-particle diffusion (IDP) model equation ($\text{mg}/(\text{g} \cdot \text{min}^{1/2})$), and C (mg/g) is a constant for intra-particle diffusion proportional to the extent of boundary layer thickness. Q_t is the sorption capacity in the time t (mg g^{-1}) and q_e is the equilibrium sorption capacity. The results of the kinetic measurements for chromium are presented in **Figure 4**. 0.2 g of the slag and 50 dm^{-3} of the solution of chromium (III) with the initial concentration of 500 mg dm^{-3} was used. The best fit was obtained for the pseudo-second order sorption model. The rate constant was $0.0000432 \text{ g mg}^{-1} \text{ min}^{-1}$.

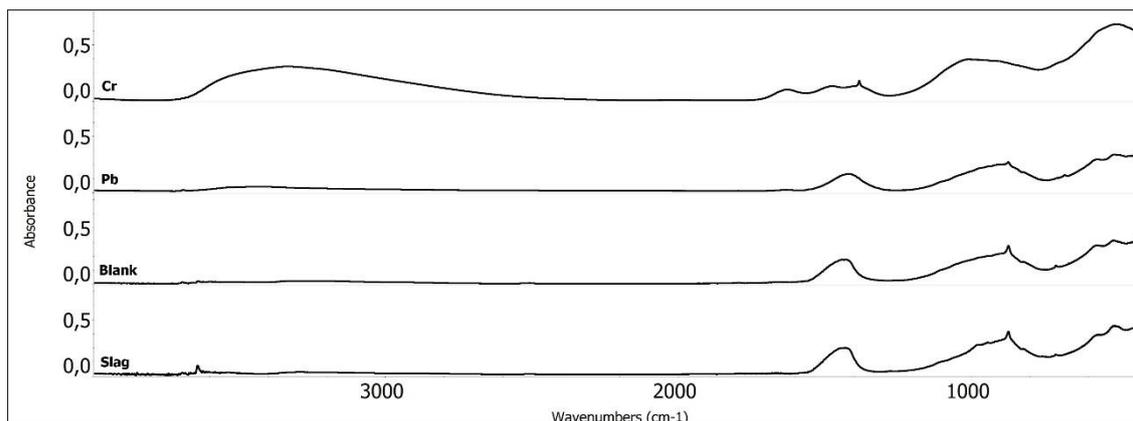


Figure 3 FTIR spectra of the slag before and after the adsorption

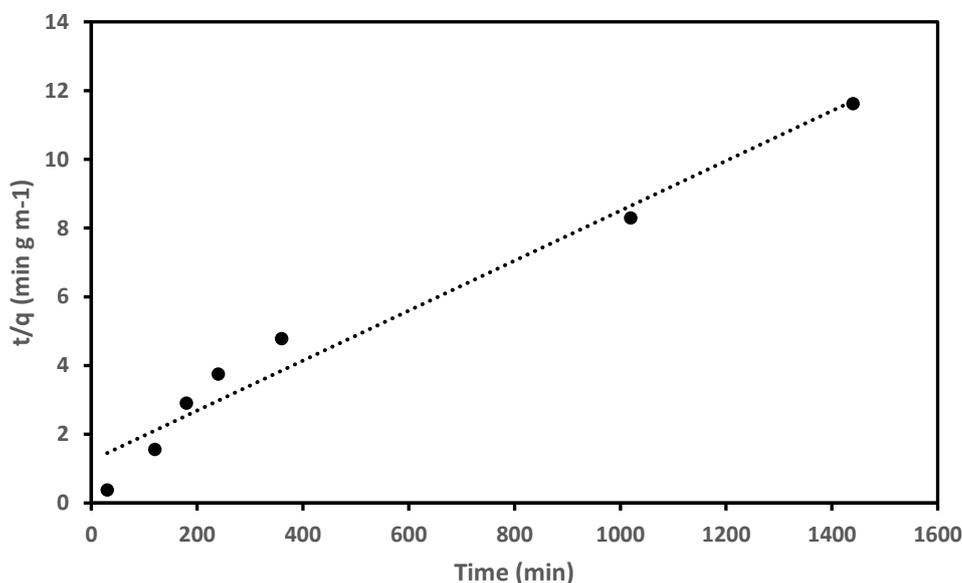


Figure 4 Application of the pseudo-second order sorption model to the kinetic data for 0.2 g of the slag and 50 dm^{-3} of the solution of chromium with the initial concentration of 500 mg dm^{-3}

The sorption capacities were evaluated according to the Freundlich isotherm (equation 4) and Langmuir isotherm (equation 5). Lead sorption proceeded according to the Freundlich isotherm (correlation coefficient 0.968) and the Freundlich equilibrium constant was 0.755 for 1g of the slag and various initial concentrations. The sorption capacities were dependent on the pH value which was increasing with the slag amount. The maximum sorption capacity for lead was about 260 mg g^{-1} (**Figure 5**). The Langmuir isotherm was more suitable for the chromium adsorption process (correlation coefficient 0.9654). The maximum sorption capacity was approximately 150 mg g^{-1} (**Figure 6**).

$$\ln q = \ln K_F + \frac{1}{n} \cdot \ln c_e \quad (4)$$

$$\frac{c_e}{q} = \frac{1}{b \cdot q_m} + \frac{1}{q_m} \cdot c_e \quad (5)$$

3. CONCLUSION

Chromium and lead removal from water solutions using the basic oxygen furnace slag was investigated. The calcium-silicate slag, which is usually deposited in dumping ground, was used for heavy metals sorption after drying, milling, and sieving. The fraction under 0.1 mm used for the leaching experiments was characterized by XRD, IR, surface, and thermal analysis. Adsorption data of chromium were correlated with the pseudo-second-order kinetic model equation. The rate constant was $0.0000432 \text{ g mg}^{-1} \text{ min}^{-1}$. Lead was adsorbed very quickly. The sorption process of lead proceeded according to the Freundlich isotherm and that of chromium according to the Langmuir isotherm. The sorption capacity over 150 mg/g was reached for chromium. The maximum sorption capacity for lead was about 250 mg/g .

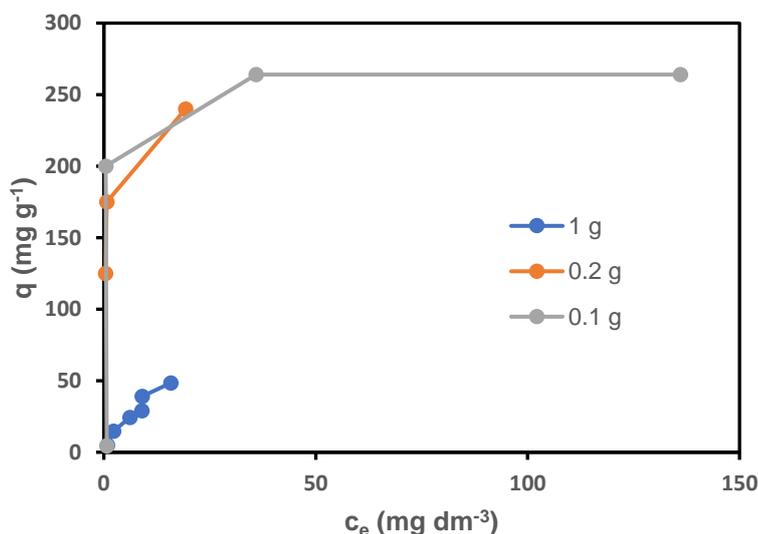


Figure 5 Adsorption of Pb(II) onto slag after 24 hours (initial concentration 10-1,000 mg dm⁻³)

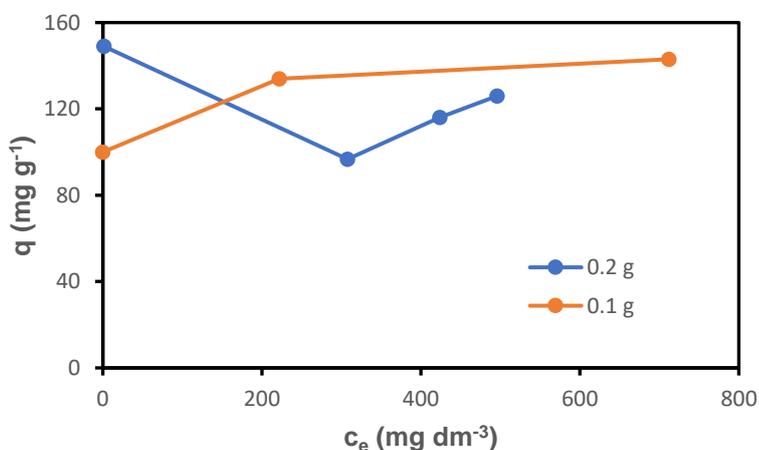


Figure 6 Adsorption of Cr(III) onto slag after 24 hours (initial concentration 200-1,000 mg dm⁻³)

ACKNOWLEDGEMENTS

This work was financially supported by the project „Research on the management of waste, materials and other products from metallurgical and related sectors “, CZ.02.1.01/0.0/0.0/17_049/0008426 and by the project of Specific research: SP2022/61.

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