Cadmium Sorption on to Basic Oxygen Furnace Slag

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ABSTRACT

Cadmium removal from water solutions using the basic oxygen furnace slag was investigated. Calcium, iron, and silica compounds were the main components of the slag. The samples were characterized by means of the thermal, surface, and mineralogical analysis and infrared spectroscopy. The sorption experiments were performed at the ambient temperature. The results showed that the cadmium adsorption proceeded according to the Langmuir isotherm. The sorption capacity over 100 mg/g was reached. The agitation slightly increased the sorption capacity of the tested slag. Kinetic data were analysed using the pseudo-first, pseudo-second and intra-particle diffusion models. The relationship between the amount of cadmium removed from the solution and calcium leached out from the slag was observed. The interchange Ca - Cd ions was determined as the basic retention mechanism.

Keywords: Cadmium; Slag; Langmuir Adsorption Isotherm; Kinetics

Introduction

Cadmium belongs among the very toxic elements. Complications of Cd poisoning include anemia, kidney failure, osteocarcinoma etc. Due to its low permissible exposure in humans, overexposure may occur even in situations where trace quantities of cadmium are found. The primary use of cadmium is in the manufacturing of NiCd rechargeable batteries (Djukić et al., 2013) [6]. Operations involving removal of cadmium paints by scraping or blasting may pose a significant hazard. Some sources of phosphate in fertilizers can also contain cadmium which can lead to an increase in the concentration of cadmium in soil and consequently in food (Qi et al., 2017) [25]. Electroplating and metal surface treatment processes generate significant quantities of wastewater containing heavy metals including cadmium (Barakat, 2011) [2]. Cadmium is also used in nuclear reactors where it acts as a neutron absorber. The conventional processes for removing heavy metals from wastewater include many processes such as chemical precipitation, adsorption, flotation, ion exchange, and electrochemical deposition. Lime and limestone precipitation is often used to retain the cadmium, but it requires further treatment of the sludge (Aziz et al., 2008, Naiya et al., 2008, Li et al., 2012) [1, 22, 17] . HCl proved to be an efficient elution agent. The adsorption capacity over 1000 mg/g can be achieved by some materials as biochar (Li et al., 2020) [16]. Inyang et al. (2016) [12] investigated the sorption kinetics of cadmium on clay minerals. Satisfactory results were obtained also for hydroxyapatite (Joshi and Manocha, 2017) [13], lower sorption capacities were reached using red mud (Luo et al., 2011) [18]. The activated calcium-silicate slag was used by Czech et al. (2018) [5] (sorption capacity about 40 mg/g) or Duan and Su (2014) [7] (10 mg/g). Competitive sorption of metals by ferronickel slag was studied by Park et al. (2016) [24]. **Activated carbon, nano-adsorbents – e.g., Fe_3O_4, po**lyacrylonitrile (PAN)–titanium oxide (TiO_2), or **zeolite can be used, too** (Barragán et al., 2017) [3]. The steel furnace slag and CeO_2 nanoparticles were tested by Mercado-Borrayo et al. (2018). Excellent results were obtained using basic oxygen furnace slag activated by the mechanochemistry process for single and coadsorption of copper, cadmium, lead and zinc as demonstrated by Xu et al., 2020. [30] Ion exchange using synthetic organic resins is usually very responsive to pH. The application of dithiocarbamated-sporopollenin lead only to the low removal rate of cadmium (Unlü and Ersoz, 2007) [28]. A nanocomposite material, consisting of nano zero valent iron and a cation exchange resin was used for heavy metals removal from contaminated water streams by Toli et al. (2021) [27]. The concentration of Cd in effluent was less than 0.04 mg/L. Membrane filtration and electrodialysis are advanced and broadly used technology for management of heavy metal contaminated wastewater (Kurniawan et al., 2006) [15]. Grimshaw et al. (2011) [8] used cyclic electrowinning and precipitation for co-removal of Cd, Cu and Ni.

The aim of this study was to verify the possibility to use such type of the steel-making slag, which has not any further exploitation, for the pre-treatment of wastewater containing heavy metals, namely cadmium.

Experimental

Materials

The initial stock solution of Cd(II) with the concentration of 1000 mg dm^{-3} was prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ 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, further filled with 50 ml of Cd(II) solutions and stirred for 0.5 – 24 hours. Most of 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 and some of the residues were dried and characterized by various methods. Several leaching experiments were performed without stirring.

Characterization methods

The content of the monitored elements in slag and in the leachates was determined using AAS (Varian AA280FS) and wavelength dispersive X-ray fluorescence spectrometry XRF (ARL PERFORM´X 4200, Thermo Fischer). In the case of XRFS, the samples were measured in the form of pressed pellets with cellulose and fused beads with lithium tetraborate flux; all measurements were carried out in vacuum.

The measurement of the specific surface area 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 5°C/min, air, sample weight 20 mg.

The crystalline phases were identified by the powder diffractometer MiniFlex600 with Co lamp 600 W, Theta / 2 Theta), Rigaku, Japan.

The infrared (IR) spectra of all 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}.

Results and Discussion

Slag characterization

The chemical composition of the steelmaking slag can be seen in Table 1. The content of cadmium was sufficiently low so this material can be used for its removal from the solutions.

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

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

The surface analysis of the slag showed that the specific surface was 6 m^2/g, the mesopores volume 0.074 cm^3/g and the micropores volume 0.003 cm^3/g. The slag can be characterized as almost non-porous.

The mineralogical composition of the original slag is shown in Figure 1a. Lime, periclase and mayenite were identified as the non-stable phases in water environment. Other phases include iron oxides, dicalcium silicate, calcium aluminoferrite and calcium-iron silicate.

Leaching Experiments

Adsorption isotherms

To verify the possibility to use the selected slag for the heavy metals' removal, a blank experiment was carried out. In this experiment, 1g of the slag was leached with 50 mL of deionized 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.
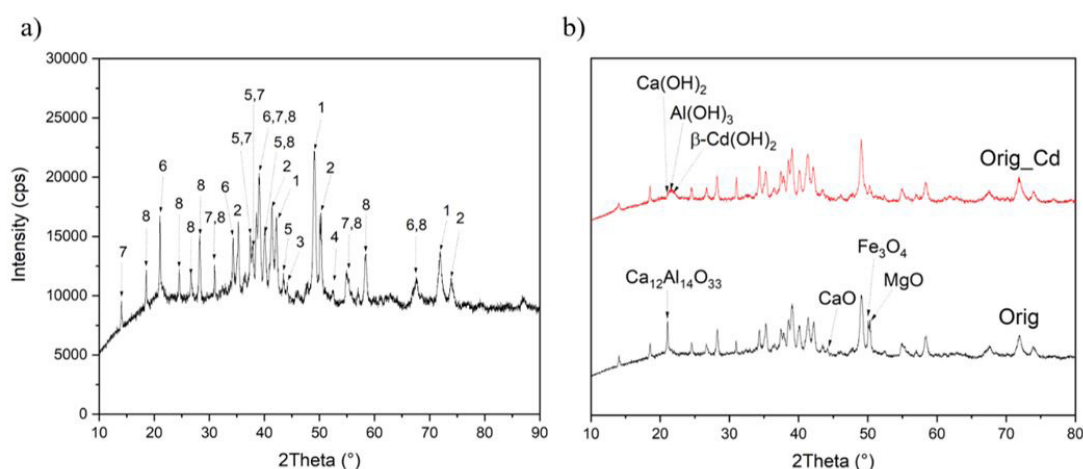

Figure 1: XRD pattern of the original steel-making slag **(a)** and comparison of the original steel-making slag (Orig) and this slag after the Cd(II) sorption (Orig_Cd) **(b).** (1 - FeO (89-0686) Wustite, 2 - Fe$_3$O$_4$ (75-0449) Magnetite, 3 - CaO (78-0649) Lime, 4 - MgO (85-5625) Periclase, 5 - Ca$_2$(SiO$_4$) (83-0464) Larnite, 6 - Ca$_{12}$Al$_{14}$O$_{33}$ (48-1882) Mayenite, 7 - Ca$_2$FeAlO$_5$ (72-7995) Brownmillerite, 8 - Ca(Fe 0.77Mg 0.22)(SiO$_4$) (87-2073) Kirschsteinite)

Then 0.1, 0.2, 0.5 and 1g of the slag was treated with the solutions of the concentration 10 – 2000 mg dm^{-3} of Cd(II). Selected results can be seen in **Fig.2** and the respective graph shows that quite high sorption capacity of the slag was reached. For 0.2 g of the slag the obtained sorption capacity was close to 100 mg of Cd(II) per 1g of the slag.

The adsorption mechanism was evaluated by Freundlich (Eq. 1), Langmuir (Eq. 2) and Dubinin-Radushkevich (Eq. 3 - 5) isotherms.

$$\ln q = \ln K_F + (1/n) \ln c_e \qquad\qquad (1)$$
$$c_e/q_e = 1/(q_{max} k_L) + c_e/q_{max} \qquad\qquad (2)$$
$$\ln q_e = \ln q_m - \varepsilon^2 K_D \qquad\qquad (3)$$
$$\varepsilon = RT \ln (1+1/c_e) \qquad\qquad (4)$$
$$E = 1/(2K_D^{0.5}) \qquad\qquad (5)$$

Q_m is the maximum amount of metal adsorbed (mg g^{-1}), c_e is the concentration of metal in the solution (mg dm^{-3}), K_F and n are the Freundlich equilibrium constants related to the free energy of adsorption, b is Langmuir adsorption constant (dm^3 g^{-1}), K_D is constant of D-R model related to the mean free energy (mol^2 kJ^{-2}), ε (kJ mol^{-1}) is the Polanyi potential. The relationship between Polanyi potential and equilibrium concentration is expressed by Eq. (4), where, R and T are the universal gas constant and the absolute temperature (K), respectively. K_D can give valuable information about the mean sorption energy E (Eq. 5). The experimental data fitted well the Langmuir isotherm. The value of q_{max} was 102 mg/g and the Langmuir constant was 0.33 dm^{-3} mg^{-1}. Neither Freundlich (1) nor Dubinin-Radushkevich (3 - 5) isotherms could be used.

The influence of agitation on the sorption capacity can be seen in Figure 3 The initial concentration of Cd(II) was 300 mg dm^{-3}. For the shorter time, the sorption capacity was slightly higher in the agitated solution, after 24 hours it was almost the same.
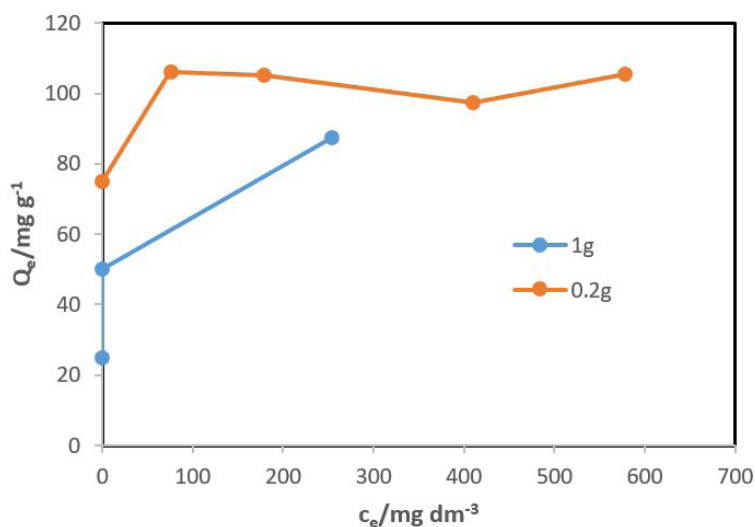

Figure 2: Adsorption of Cd(II) onto slag after 24 hours (initial concentration 300-2000 mg dm^{-3})
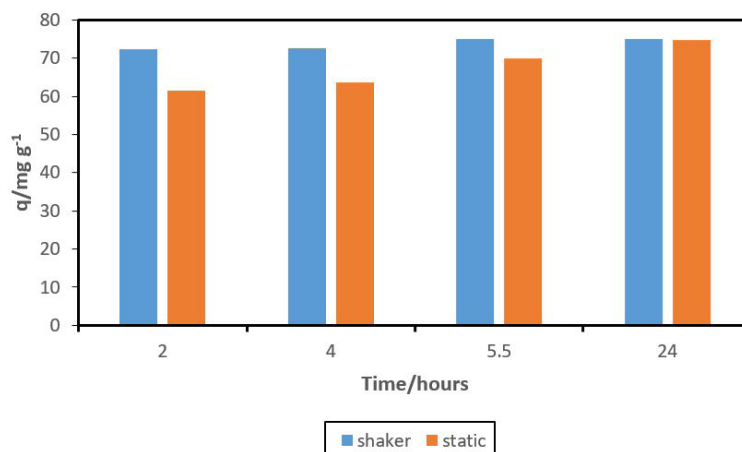

Figure 3: Effect of agitation on the sorption capacity – 0.2 g of slag, 300 mg/l Cd (II)

Adsorption kinetics

The adsorption kinetics was studied for 0.2 g of the slag and 50 ml of the solution with the concentration of 600 mg dm^{-3}. The preliminary experiments proved that no significant amount of Cd was removed from the solution after more than 24 hours.

The kinetic behaviour was evaluated by a pseudo-first order (Eq. 6), pseudo-second order (Ho et al., 2000) (Eq. 7) and intra-particle diffusion (Li et al., 2020) (Eq. 8) models.

$$\ln(q_e - q_t) = lnq_e - k_1 t \tag{6}$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \tag{7}$$

$$q_t = k_i t^{0.5} + C \tag{8}$$

K_1(min^{-1}) is the rate constant for the pseudo first-order model equation, k_2 (g/(mg min)) is the rate constant for pseudo-second-order kinetic model equation, k_{id} is the rate constant of the intra-particle diffusion (IDP) model equation (mg/(g・min$^{1/2}$)), and C (mg/g) is a constant for intra-particle diffusion proportional to the extent of boundary layer thickness. The best fit was obtained for the pseudo-second-order kinetic model (Figure 4, R^2 value >0.99). The rate constant was 0.000191 g mg^{-1} min^{-1}. Other models did not provide the linear dependences. The pseudo-second-order kinetic model is considered as the diffusion-controlled model indicating the chemisorption as the rate-limiting step and is often applied in the description of heavy metals adsorption onto different adsorbents (Huang et al., 2015; Kołodynska et al., 2012; Módenes et al., 2015) [11, 14, 21] . In the IPD model, the rate limiting step is the transport of metal ions from the solution into the pores of slags (Czech et al., 2018) [5]. Because the slag under investigation is not very porous, the usability of this model could not be expected. The model based on the exchange of cations with slag is more presumptive.
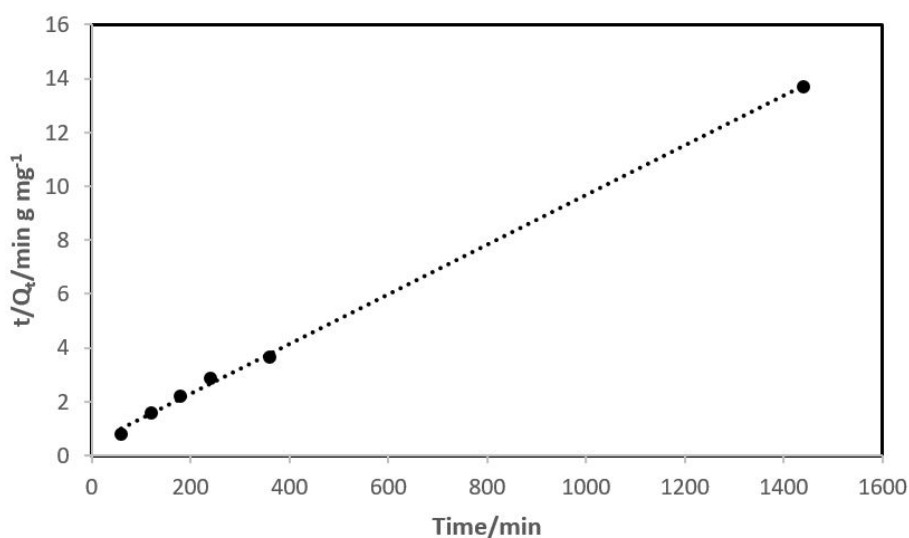

Figure 4: Application of the pseudo-second order sorption model to the kinetic data for 0.2g of the slag and 50 dm^{-3} of the solution of cadmium with the initial concentration of 600 mg dm^{-3}

To elucidate the sorption mechanism, various methods were used. The results of the FTIR analysis can be seen in Figure 5. The difference in the samples before and after cadmium sorption can be seen mainly in the range 3700-3300 cm^{-1}. The spectral bands above 3000 cm^{-1} belong to stretching vibration of hydroxyl group of water. According to wavenumbers of the bands, we can predict different types of water present in the samples. The weak and narrow bands above 3600 cm^{-1} (3643 cm^{-1} in the *slag* sample of the; 3695 cm^{-1} and 3643 cm^{-1} in *blank*; 3695 cm^{-1} and 3608cm^{-1} in the sample *Cd*) can be assigned to O-H stretching vibration of water in lattice of inorganic compounds (inorganic hydrates). The wavenumber of the hydrates of inorganic compounds is affected by anion presented in hydrates (Horák and Papoušek; 1976) [10]. In the spectrum of sample *Cd*, the very broad band at 3460 cm^{-1} is assigned to stretching vibration of O-H of physical adsorbed water (Horák and Papoušek; 1976) [10].

The spectral bands below 2000 cm⁻¹ were assigned as follow. The bands at 1448 cm⁻¹ (E'), 874 cm⁻¹ (A₂"), and 714 cm⁻¹ (E') are due to vibration of carbonates (CO_3^{2-}). The data in parentheses indicate the group of symmetry mentioned vibrations. A weak shoulder at 1386 cm⁻¹ (in the spectrum of sample **Cd**) belongs to stretching vibration of nitrates (NO_3^-); group symmetry E'.

The rest of bands marked by wavenumbers can be very probably assigned to iron oxides or oxyhydroxides. The bands just above 900 cm⁻¹ could be attributed to deformation vibration of O-H in iron oxides/oxyhydroxides (Bell et all., 1995; Weckler and Lutz, 1998) [4, 29]. These bands are present in spectrum of **slag** sample (984 cm⁻¹ and 945 cm⁻¹) and in spectrum of sample **Cd** (978 cm⁻¹). The bands at 569 cm⁻¹ and 510 cm⁻¹ could be belong to deformation vibration of Fe-O lattice. We suppose there are Fe-O vibrational transitions in the hematite close packed structure (Bell et all., 1995) [4].
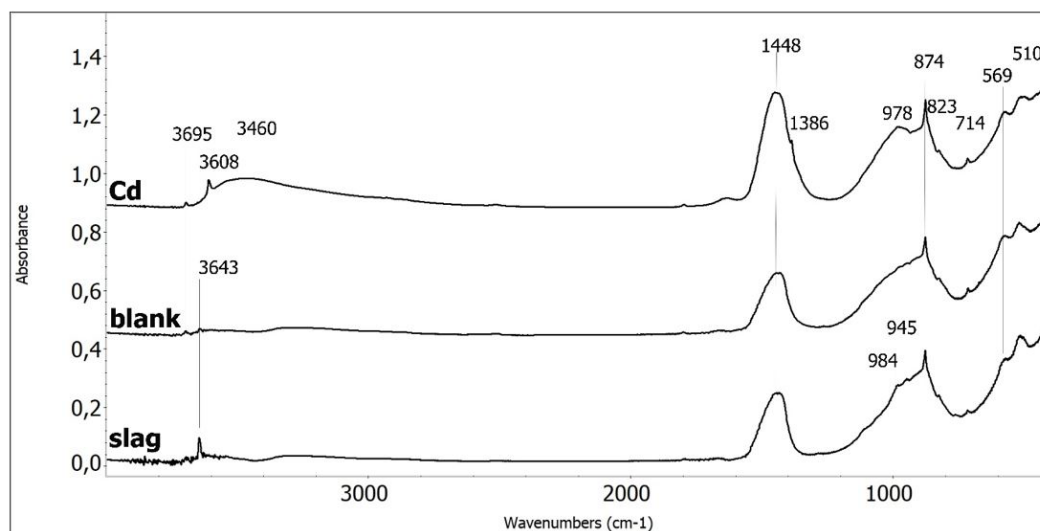

Figure 5: FTIR spectra of the slag before and after sorption

Figure 6 presents the results of the thermal analysis. The firs 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 weight loss for the slag with adsorbed Cd was much higher. Cadmium probably replaced calcium from the slag and its compounds decomposed more easily. The second mass loss starting at 640°C can be attributed to the decomposition of $CaCO_3$. Lime 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 XRD analysis on sample of slag after the sorption experiment can be seen in Figure 1b. As visible from Figure 1b, lime and mayenite were dissolved during the sorption experiments and their poorly crystalline hydroxides originated. The chemical analysis of the solutions after the sorption experiments (Figure 7) revealed that the amount of cadmium removed from the solution increases with the amount of calcium leached out of the slag.
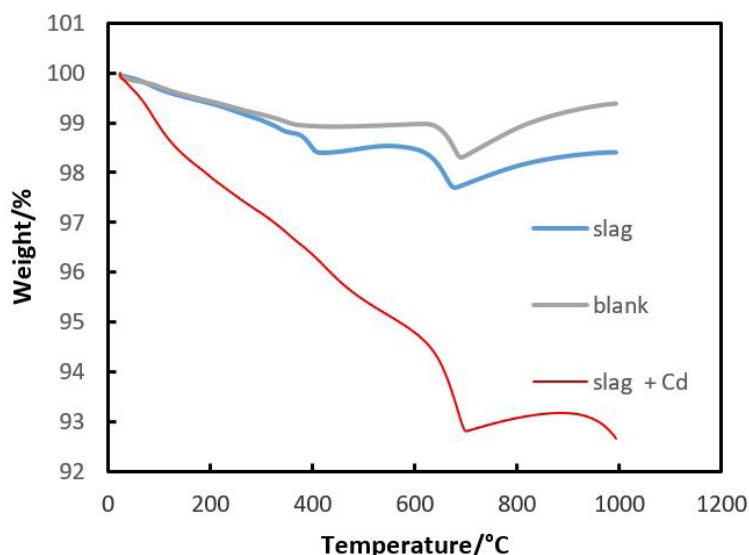

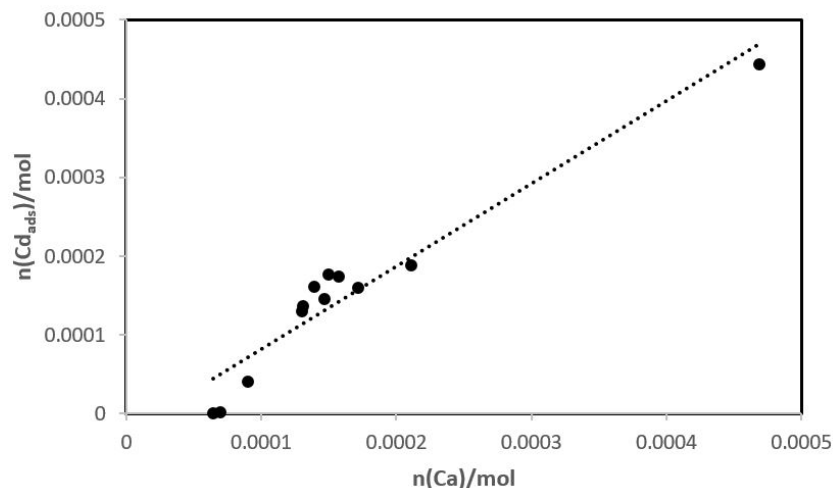**Figure 6:** Thermal analysis of the slag before and after cadmium sorption

Figure 7: Relationship between the amount of cadmium removed from the solution and calcium leached out from the slag

Conclusions

Cadmium 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 cadmium 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 were strongly correlated with the pseudo-second-order kinetic model equation and the Langmuir adsorption isotherm. The sorption capacity over 100 mg/g was reached. The rate constant for the solution of 600 mg dm^{-3} of Cd(II) was 0.000191 g mg^{-1} min^{-1}. A linear relationship between the amount of cadmium removed from the solution and calcium leached out from the slag was found. Calcium – cadmium exchange is a probable mechanism of the metal removal from the solution, as can be seen from the results of the XRD, IR, and thermal analysis.

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Acknowledgements

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