International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:11, No:11, 2017

Reduction of Content of Lead and Zinc from Wastewater by Using of Metallurgical Waste

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***Abstract*—**The aim of this paper was to study the sorption properties of a blast furnace sludge used as the sorbent. The sorbent was utilized for reduction of content of lead and zinc ions. Sorbent utilized in this work was obtained from metallurgical industry from process of wet gas treatment in iron production. The blast furnace sludge was characterized by X-Ray diffraction, scanning electron microscopy, and XRFS spectroscopy. Sorption experiments were conducted in batch mode. The sorption of metal ions in the sludge was determined by correlation of adsorption isotherm models. The adsorption of lead and zinc ions was best fitted with Langmuir adsorption isotherms. The adsorption capacity of lead and zinc ions was 53.8 $mg.g^{-1}$ and 10.7 $mg.g^{-1}$, respectively. The results indicated that blast furnace sludge could be effectively used as secondary material and could be also employed as a low-cost alternative for the removal of heavy metals ions from wastewater.

***Keywords*—**Blast furnace sludge, lead, zinc, sorption.

I. Introduction

CONTAMINATION of water by heavy metals through the discharge of wastewater is a worldwide environmental problem. Industrialization has seriously contributed to the release of heavy metals to water streams, ground water, and soils. Metals such as lead and zinc are evaluated as hazardous heavy metals for people and environment [1].

A blast furnace sludge (BFS), generated by the metallurgy industry have been tested as metal sorbents for aqueous solutions [2], [3]. The BFS is a by-product of the steelmaking industry, which is generated during the manufacture of the pig iron process from wet gas cleaning. The dried BFS consists of iron oxides (45±50 wt.%). The literature mentioned that iron oxide could affect the concentration of same metals during leaching tests [4], [5]. Its high content of iron oxide and coke may enable its use as a metal sorbent in industrial wastewater purification processes [2].

Removal of metal ions from water and wastewater in an effective way has become an important for the research. The Precipitation and coagulation has been extensively employed for the removal of heavy metals from water. However, this process usually produces large volumes of waste sludge consisting small amounts of heavy metals [6], [7]. Another way to remove metal ions is a membrane filtration, but its high cost limits the use in practice. The adsorption is one of the most effective processes of advanced wastewater treatment. The adsorption process is environmentally and economically attractive [8]. Price, availability, adsorption capacity, and strong affinity to pollutants are limiting factors for the sorbent application in the wastewater treatment, hence new materials to be used as sorbents are evaluated constantly [9].

The aim of this study was to evaluate the adsorption abilities of the BFS and its application for the removal of metal ions from wastewater. The experiments were focused on the removal of Pb and Zn ions from aqueous solutions.

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II. Materials and Methods

A. Materials

The sorbent BFS sample used in this study was obtained from process of iron making. BFS is a co-product generated after the blast furnace gas is washed to separate solid particulates as sludge. BFS sample has been separated into size fractions using sieve analysis before the characterization and the sorption experiment. This material is a powder of a particle size up to 0.8 mm. For the chemical analysis, a representative sample of the sludge was obtained by treatment with demineralized water for 24 hours. According to EU standard 200/532/EC list of the hazardous waste, this waste belongs to the category of the waste from iron and steel industry, and in the European Waste List, it is listed as No. 100214 - sludges and filter cakes from gas treatment [9].

B. Analytical Methods

The mineralogical structure was determined by means of X-ray powder diffraction on the powder diffractometer D8 ADVANCE (BRUKER) with the detector Vantec. The chemical composition was determined by using fully automatic sequential X-Ray fluorescence spectrometer SPECTRO X-LAB (SPECTRO Analytical Instruments GmbH. For XRFS measurement, the powder form sample was pressed into tablets using a wax binder. The morphological analysis of the sludge was performed by scanning electron microscopy (SEM Philips XL-30). The specific surface area was measured with the Sorptomatic 1990 device using nitrogen gas and calculated by the Advance Data Processing software according to the BET isotherm. The concentration of metal ions in aqueous solutions was determined by means of the atomic absorption spectrometer FA-AAS (UNICAM 969).

C. Sorption Experiment

The sorption properties of BFS were evaluated using a model of metal ions of lead and zinc in a model solution. The sorption properties of the BFS were studied in the batch mode. Blank systems (without the addition of solids) were prepared, too. Vials were sealed and continuously stirred in a shaker

device. The reaction time was 1 hour. Sampling of sludge was employed for the sorption experiments carried out with the 1 g of sorbent suspended in the 50 ml model solution of various metal concentrations (50 – 2000 mg.l^{-1}) at the laboratory temperature. The model solutions of metal ions were prepared by dissolving the corresponding amount of nitrate in demineralized water for the adsorption experiment. Model solutions were prepared from $Pb(NO_3)_2$ and $Zn(NO_3)_2$. After elapsing the contact time, the vials were filtered using 0.45 µm pore size membrane filter Millipore. Then, nitric acid conservation was applied, and the metal concentration was determined by means of FA-AAS. The quantity of the adsorbed metal ion of the sludge was calculated as the difference between the initial concentration and the concentration at equilibrium. The concentration of metal ions sorbed onto the solid was calculated using (1):

$$q = \frac{c_0 - c}{m_{ads}} \quad (1)$$

where c_0 and c are the metal concentrations in liquid phase before and after the adsorption experiments (mg.l^{-1}), respectively, and m_{ads} is the mass of the adsorbent in the solution (g).

Using the sorption isotherm models, the relationship between the sludge adsorption capacity and the metal cation concentration at equilibrium was analyzed.

III. Results and Discussion

A. Characterization of Sorbent

Macroscopically, BFS sorbent is a dark grey in color when moist and a light grey when dry.

The BFS is a complex heterogeneous material composed mainly of the hematite (α-Fe_2O_3) and the magnetite (Fe_3O_4) as shows Fig. 1. The sorbent is composed of both organic and inorganic compounds. The organic part comprises the carbonaceous matrix and the inorganic matter. The chemical analysis of the sorbent is shown in Table I. Sorbent is a complex heterogeneous material composed mainly of iron and calcium. Sorbent pH value was 11.0.

TABLE I
Chemical Composition of BFS Expressed in Oxides

Elements	Unit	BFS	Elements	Unit	BFS
Na_2O	[%]	0.67	K_2O	[%]	0.10
MgO	[%]	1.21	CaO	[%]	3.22
Al_2O_3	[%]	0.71	TiO_2	[%]	0.05
SiO_2	[%]	0.71	MnO	[%]	0.26
P_2O_5	[%]	0.10	Fe_2O_3	[%]	62.0
SO_3	[%]	0.61			

X-ray diffraction pattern is shown on Fig. 1. X-ray diffraction (XRD) data confirm that the phase composition of the sorbent is a mixture of Fe(II,III)O, calcium carbonate, α-SiO_2, and the cristobalite. The sample was polycrystalline containing five different crystal phases in various amount and crystallinity levels. The major phases were identified as the hematite and the magnetite. In the powder sample, small traces of elementary iron (α-Fe, bcc) were found. The sample contained high concentration of iron and calcium.

Using microcopy the solid phases were analyzed and texture of surface was determine. Fig. 2 shows the observation of the solid phase of the sorbent. It is apparent that the sorbent consist from a combination of spherical particles which are heterogeneous in the shapes and sizes.

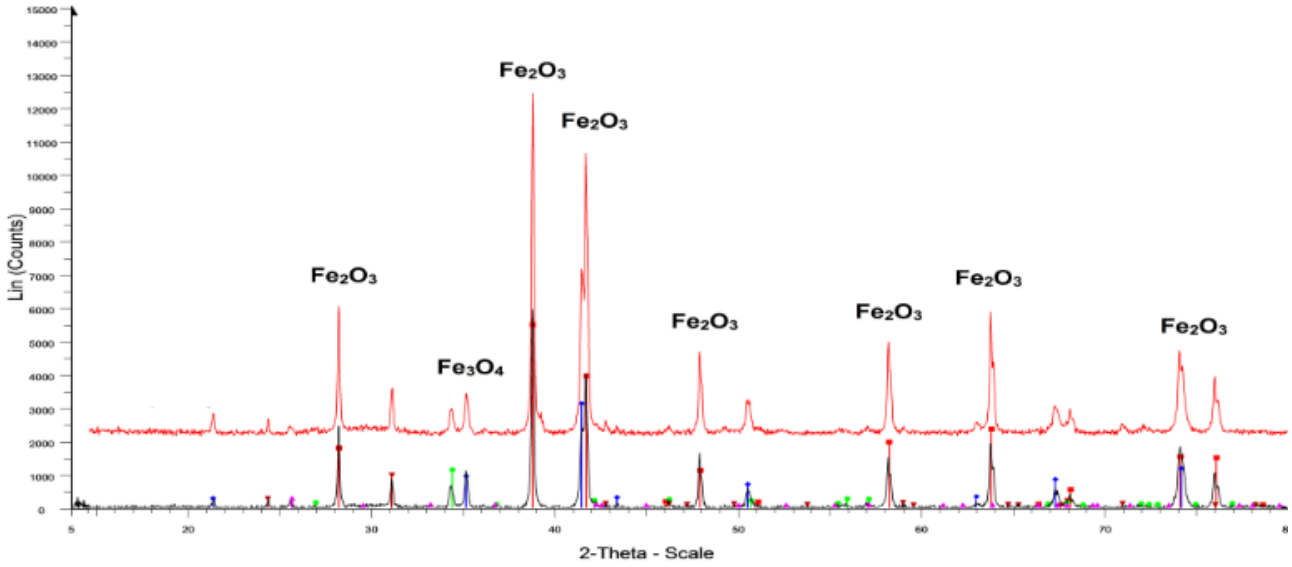

Fig. 1 X-Ray diffraction pattern of preliminary BFS is the lower curve, and the treated BFS is the upper curve (red)

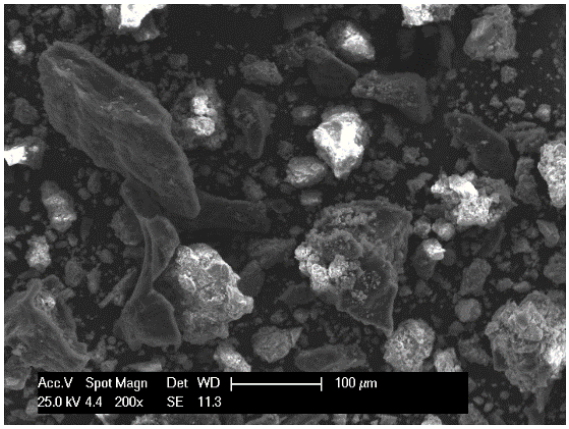

Fig. 2 SEM image of BFS showing of material texture

B. Sorption Experiments

It is important to establish the adsorption isotherm, which is a reliable prediction of adsorption parameters and quantitative comparison of adsorbent behavior for different adsorbent systems and conditions. Experimental data of sorption of Pb and Zn ions were processed by the Langmuir [10], Freundlich [11], Temkin [12], Dubinin-Radushkevich (D-R) [13] isotherms. Langmuir isotherm can be linearized by the four different ways [14]. Determination coefficient of linear regression analysis (R^2) represents the proportion of the dependent variable expressed by the regression line. Regression coefficient was used to determine the best corresponding adsorption isotherm.

The Langmuir isotherm model describes uptake occurs on the homogeneous surface by monolayer sorption without interaction between adsorbent molecules and the model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter (R_L), which is defined by (2):

$$R_L = \frac{1}{1+Kc_i} \quad (2)$$

where b is the Langmuir constant, c_i is the initial concentration. The R_L value indicates the shape of the isotherm:

- $R_L = 0 \rightarrow$ irreversible,
- $0 < R_L < 1 \rightarrow$ favorable,
- $R_L = 1 \rightarrow$ linear,
- $R_L > 1 \rightarrow$ unfavorable isotherm [15], [16].

The Freundlich isotherm model describes the relationship between non-ideal and reversible adsorption which is applied to adsorption on the heterogeneous surface with the interaction between adsorbed molecules. The Dubinin-Radushkevich isotherm model is used to evaluate the nature of sorption process and the mean energy of sorption. The Temkin isotherm contains a factor that describes of relationship between adsorbent-adsorbate and by ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage. All the parameters of adsorption isotherm models were calculated in Table II.

The amount of the adsorbed metal ion per sorbent unit q_e was calculated from the metal concentration in liquid phase before adsorption and the unadsorbed metal concentration in solution at equilibrium c_e. Fig. 3 presents the amount of Pb(II) and Zn(II) ions sorbed per unit mass of material plotted against the concentration of Pb and Zn remaining in model metal solution after reaching equilibrium.

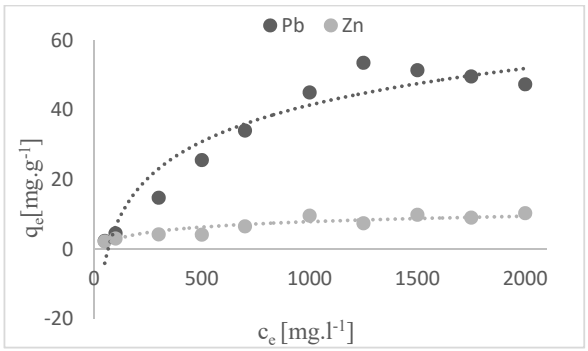

Fig. 3 The amount of Pb(II) ions and Zn(II) ions adsorbed per unit mass of material in model solution of metal

Fig. 4 shows the values of the separation factor. The value of RL in both cases for all the concentrations lies between 0-1. It shows that the sorption of Pb(II) and Zn(II) onto the surface of BFS is favorable. The value of Pb(II) and Zn(II) ions decreases with the increase in concentration indicating favorable adsorption at lower concentration.

Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich adsorption isotherms are plotted in Figs. 5-8, respectively. In terms of R2 values, the applicability of the above models for present experimental data approximately followed the order: Pb: Langmuir I > D–R> Temkin > Freundlich > Langmuir II > Langmuir III and IV; Zn: Langmuir I > Freundlich > Temkin > Langmuir II > Langmuir III and IV > D–R.

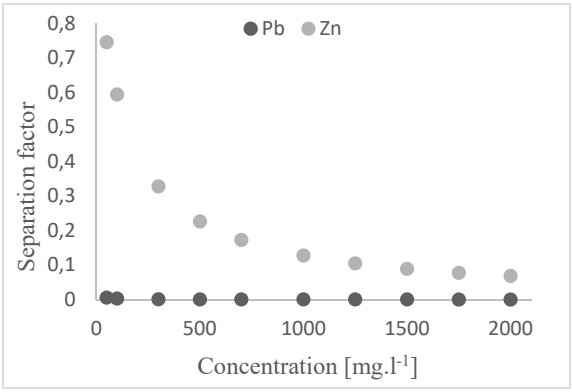

Fig. 4 Separation factor of Pb(II) and Zn(II) ions

TABLE II
ISOTHERMS PARAMETERS OBTAINED BY USING LINEAR REGRESSION

Adsorption isotherms	Isotherm constants	Pb	Zn
	q_m	48.08	10.68
Langmuir I	K_L	3.586	0.007
	R^2	**0.999**	**0.966**
	q_m	53.76	1.141
Langmuir II	K_L	3.957	6.669
	R^2	0.7103	0.864
	q_m	-4.160	-0.132
Langmuir III	K_L	-0.006	-0.914
	R^2	0.3989	0.531
	q_m	-0.603	-14.25
Langmuir IV	KL	-0.017	-0.111
	R^2	0.3989	0.531
	K_F	2.801	1.184
Feundlich	n	3.862	3.928
	R^2	0.8365	0.925
	b_T	502	1853
Těmkin	A_T	59,68	0.684
	R^2	0.9466	0.8275
	q_D	1956E18	1917
Dubinin-Radushkevich	K_D	1.021E-06	9.314E-06
	R^2	0.975	0.332

The comparison between the experimental specific uptake for different initial concentration of Pb(II) and Zn(II) ions in various equilibrium isotherm model shows that Langmuir isotherm model is best agreed with experimental data in case of BFS. The results indicate that adsorbate forms a monolayer on the outer surface of adsorbent. Maximum monolayer coverage capacities calculated from linearized type II of Langmuir isotherm of Pb(II) and Zn(II) ions are 48.08 $mg.g^{-1}$ and 10.68 $mg.g^{-1}$, respectively. Langmuir constant K_L indicates that the adsorbed ions attracted to a surface. Pb(II) ions are strongly attracted to the surface, and these ions form stronger bonds on surface than Zn(II) ions.

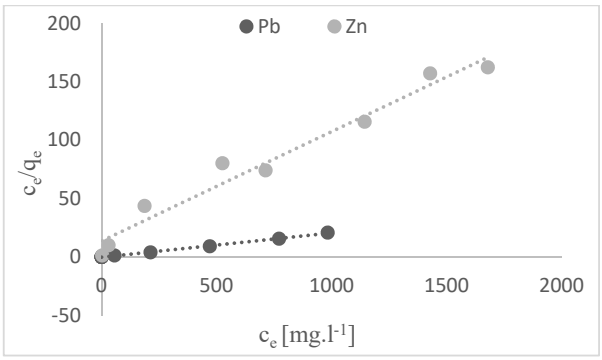

Fig. 5 Pb(II) and Zn(II) adsorption plotting of Langmuir isotherm

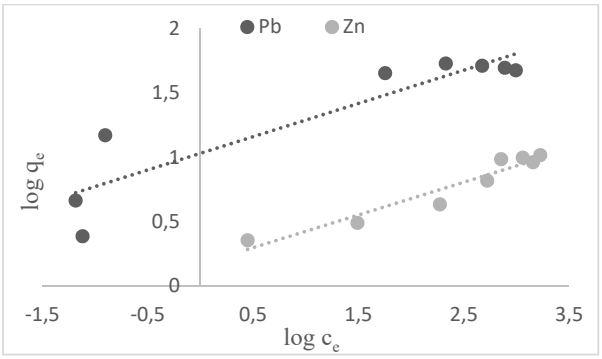

Fig. 6 Pb(II) and Zn(II) adsorption plotting of Freundlich isotherm

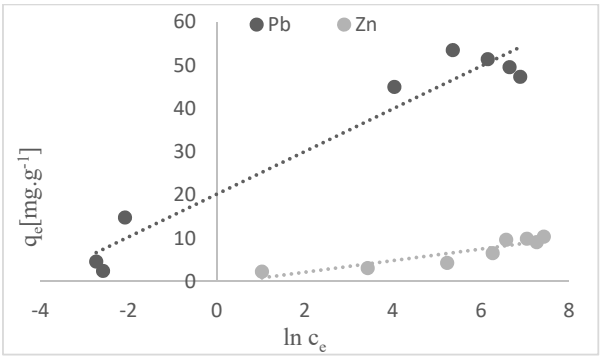

Fig. 7 Pb(II) and Zn(II) adsorption plotting of Temkin isotherm

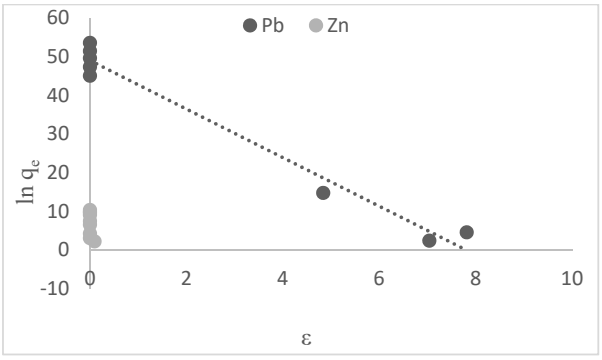

Fig. 8 Pb(II) and Zn(II) adsorption plotting of Dubinin-Radushkevich isotherm

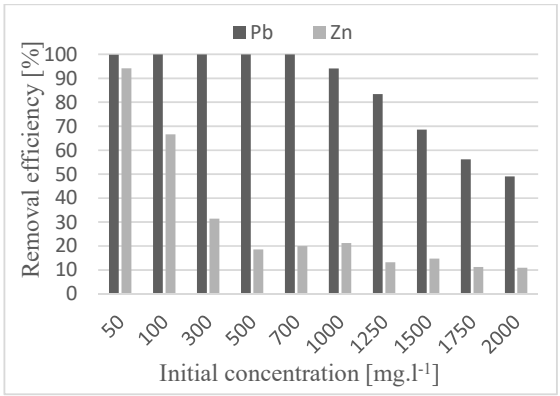

Fig. 9 Removal efficiency of Pb(II) and Zn(II) ions

Fig. 9 shows the relationship between the initial concentration and efficiency of the metal removal. When the initial concentration of Pb(II) ions from 50 $mg.l^{-1}$ to 700 $mg.l^{-1}$ then the removal efficiency is reached almost 100%. When the initial concentration has been increased then removal efficiency has been reduced. Removal efficiency of Zn(II) is better for lower concentration. The best removal efficiency of Zn(II) ions was reached with using the concentration of 50 $mg.l^{-1}$.

IV. Conclusion

The BFS was used to study the sorption properties of which were studied. The results of experiments show that it is a suitable and effective material for the sorption of Pb(II) and Zn(II) ions from aqueous solutions. The adsorption data corresponded with linearized form of the Langmuir type I isotherm. Adsorption parameters for the isotherm were determined with maximum monolayer coverage capacity of Pb(II) and Zn(II) were 48.08 $mg.g^{-1}$ and 10.68 $mg.g^{-1}$, respectively. The results indicate that the adsorbate formed a monolayer on the outer surface of adsorbent, and that no further adsorption took place.

The adsorption process for removal of Pb(II) and Zn(II) ions from aqueous solution reached high efficiency at higher concentration for Pb(II) ions and for Zn(II) ions at lower concentrations.

The BFS provides high efficiency for the removal of lead and zinc ions, and BFS could be employed as a promising low-cost adsorbent for the removal of heavy metals from aqueous solutions.

Acknowledgments

Authors thank to the financial support of the Ministry of Education, Youth and Sport Czech Republic Project LQ1603 (Research for SUSEN). This work has been realized within the SUSEN Project (established in the framework of the European Regional Development Fund (ERDF) in project CZ.1.05/2.1.00/03.0108 and TAČR – Gama project TG02010037.

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