

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

L. Rozumová, J. Seidlerová

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 XRF 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 $53.8 \text{ mg}\cdot\text{g}^{-1}$ and $10.7 \text{ mg}\cdot\text{g}^{-1}$, 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 ($45\pm 50 \text{ wt.}\%$). The literature mentioned that iron oxide could affect the concentration of some 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.

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 XRF 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

Lucia Rozumová is with the Centrum výzkumu Rez, Husinec-Rez, Czech Republic, 250 68, Czech Republic (e-mail: lucia.rozumova@cvrez.cz).

Jana Seidlerová is with the Nanotechnology Centre, VŠB - Technical University of Ostrava, 708 33, Czech Republic.

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(NO₃)₂ and Zn(NO₃)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 c₀ 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-Fe₂O₃) and the magnetite (Fe₃O₄) 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 ₂ O	[%]	0.67	K ₂ O	[%]	0.10
MgO	[%]	1.21	CaO	[%]	3.22
Al ₂ O ₃	[%]	0.71	TiO ₂	[%]	0.05
SiO ₂	[%]	0.71	MnO	[%]	0.26
P ₂ O ₅	[%]	0.10	Fe ₂ O 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-SiO₂, 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 microscopy 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.

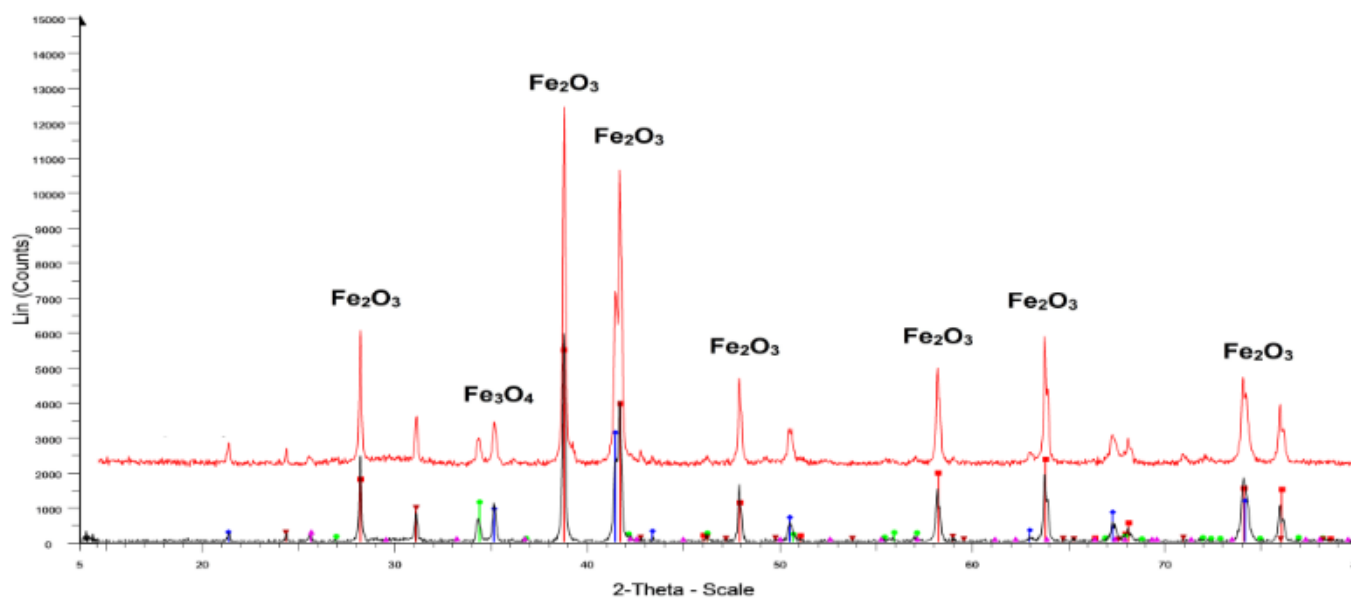


Fig. 1 X-Ray diffraction pattern of preliminary BFS is the lower curve, and the treated BFS is the upper curve (red)

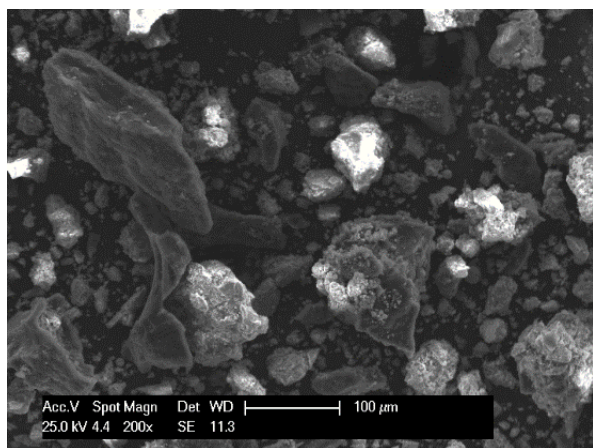


Fig. 2 SEM image of BFS showing of material texture

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.

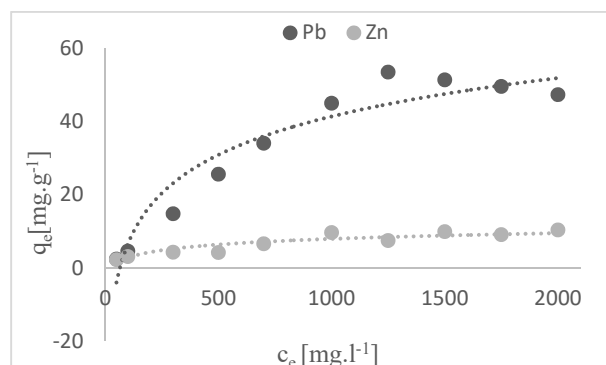


Fig. 3 The amount of Pb(II) ions and Zn(II) ions adsorbed per unit mass of material in model solution of metal

Fig. 4 shows the values of the separation factor. The value of R_L 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 R^2 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.

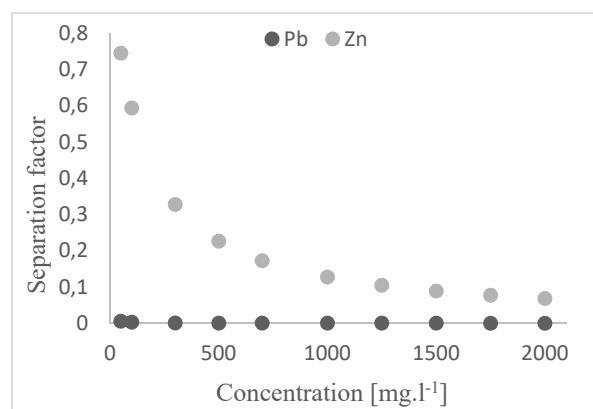


Fig. 4 Separation factor of Pb(II) and Zn(II) ions

TABLE II
 ISOTHERMS PARAMETERS OBTAINED BY USING LINEAR REGRESSION

Adsorption isotherms	Isotherm constants	Pb	Zn
Langmuir I	q_m	48.08	10.68
	K_L	3.586	0.007
	R^2	0.999	0.966
Langmuir II	q_m	53.76	1.141
	K_L	3.957	6.669
	R^2	0.7103	0.864
Langmuir III	q_m	-4.160	-0.132
	K_L	-0.006	-0.914
	R^2	0.3989	0.531
Langmuir IV	q_m	-0.603	-14.25
	K_L	-0.017	-0.111
	R^2	0.3989	0.531
Feundlich	K_F	2.801	1.184
	n	3.862	3.928
	R^2	0.8365	0.925
Tëmkin	b_T	502	1853
	A_T	59.68	0.684
	R^2	0.9466	0.8275
Dubinin-Radushkevich	q_D	1956E18	1917
	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 $48.08 \text{ mg}\cdot\text{g}^{-1}$ and $10.68 \text{ mg}\cdot\text{g}^{-1}$, 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.

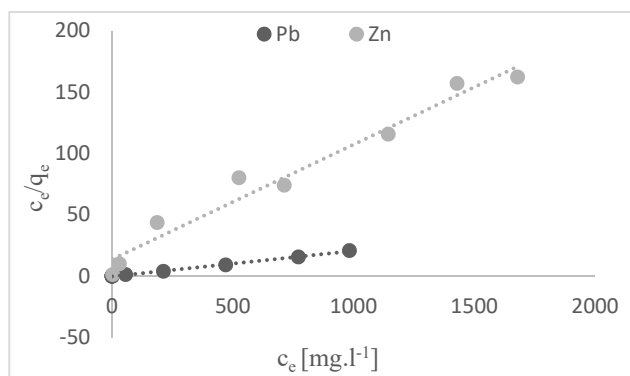


Fig. 5 Pb(II) and Zn(II) adsorption plotting of Langmuir isotherm

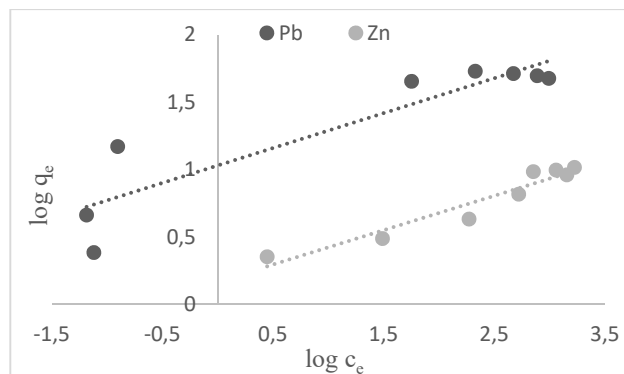


Fig. 6 Pb(II) and Zn(II) adsorption plotting of Freundlich isotherm

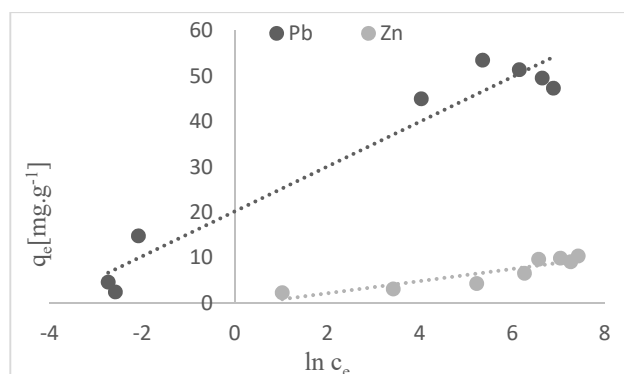


Fig. 7 Pb(II) and Zn(II) adsorption plotting of Temkin isotherm

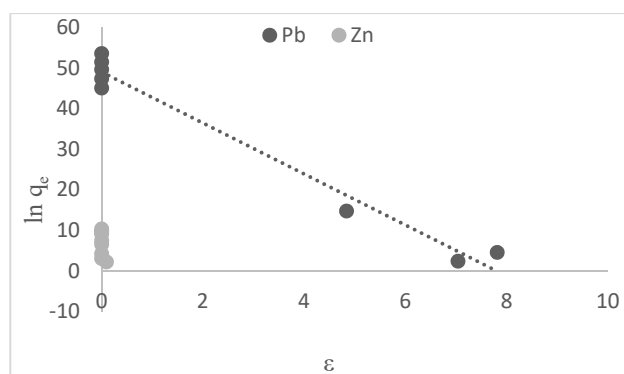


Fig. 8 Pb(II) and Zn(II) adsorption plotting of Dubinin-Radushkevich isotherm

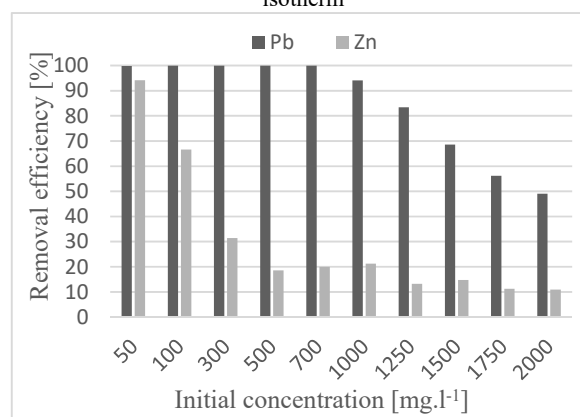


Fig. 9 Removal efficiency of Pb(II) and Zn(II) ions

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.

REFERENCES

- [1] M., Ahmaruzzaman, "Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals", *Adv. Colloid Interface Sci.*, vol. 166, pp. 36-59, 2011.
- [2] S.V., López-Delgado, "Sorption of heavy metals on blast furnace sludge," *Wat. Res.*, vol. 32, pp. 989-996, 1998.
- [3] A., Dimitrova, "Metal sorption on blast furnace slag," *Wat. Res.*, vol. 30, pp. 228-232, 1995.
- [4] J., Seidlerová, "Metody hodnocení metalurgických odpadů," Repronis Ostrava, 2009, ISBN 978-80-7329-216-4.
- [5] B. R., Coughlin, "Nonreversible adsorption of divalent metal ions (MnII, CoII, NiII, CuII, and PbII) onto goethite: effects of acidification FeII addition, and picolinic acid addition," *Environ. Sci. Technol.*, vol. 29, 1995, pp. 2445-2455.
- [6] F. A., López, "Removal of copper ions from aqueous solutions by a steelmaking by-product," *Wat. Res.*, vol. 37, 2003, pp. 3883-3890.
- [7] L., Rozumová, "Magnetically modified peanut husks as an effective sorbent of heavy metals," *J. Environ. Chem. Eng.*, vol. 4, pp.549-555, 2016.
- [8] R. A., Corbitt, "Standard hand book of environmental engineering (2nd

ed)," McGraw Hill, 1999, ISBN 9780070131606.

- [9] O. S. Amuda, "Performance optimization of coagulant/flocculant in the treatment of wastewater from a beverage industry," *J. Hazard. Mater. B*, vol. 129, pp. 69-72, 2006.
- [10] J. Langmuir, "Adsorption of gases on plane surfaces of glass, mica, and platinum," *J. Am. Chem. Soc.*, vol. 40, 1918, pp. 1361-1403.
- [11] H. M. F. Freundlich, "Über die adsorption in Lösungen," *Z. Phys. Chem.*, vol. 57, 1906, pp. 385-470.
- [12] S.D. Faustt, "Adsorption Processes for Water Treatment," Butterworth, Stoneham, MA, 1987.
- [13] S. Kundu, "Arsenic adsorption onto iron oxide-coated cement: regression analysis of equilibrium data with several isotherm models and there optimization," *Chem. Eng. J.*, vol. 122, 2006, pp. 93-106.
- [14] A. Kumar, "Alkali-treated straw and insoluble straw xanthate as low cost adsorbent for heavy metal removal. Preparation, characterization and application," *Bioresour. Technol.*, vol. 1, 2007, pp. 133-142.
- [15] N. A., Fathy, "Equilibrium removal of Pb (II) Ions from aqueous solution onto oxidized-KOH-activated carbons," *Carbon Letters*, vol. 12, 2011, pp. 1-7.
- [16] K. R., Hall, "Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions," *Ind. Eng. Chem. Fund.*, vol. 5, 1966, pp. 212-223.