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PREPARATION OF SORBENT WITH A HIGH ACTIVE SORPTION SURFACE BASED ON BLAST FURNACE SLAG FOR PHOSPHATE REMOVAL FROM WASTEWATER

A new method has been presented, which leads to a significant improvement of the adsorption ability of blast furnace slag (BFS). An ultra-high pressure water jet mill cavitation disintegrator and a controlled vacuum freeze dryer were used to disintegrate amorphous BFS. Specific surface areas of both BFS and disintegrated slag (BFS-D) were measured using the S^{BET} method. BFS-D was obtained with an average particle size of 198 nm and with 27-times bigger free specific surface area than that of original BFS. The BFS-D was tested as an adsorbent of phosphate from aqueous solutions. Adsorption data were analysed using the Freundlich and Langmuir adsorption isotherms. The BFS-D after phosphate adsorption was characterized using FTIR. The theoretical adsorption capacity of the BFS-D was 30.49 mg P/g, which represents an increase by 126.7% compared to the original BFS. Surface precipitation of hydroxyapatite was dominant retention mechanism.

1. INTRODUCTION

Adsorption is considered an effective, efficient, and economic method for wastewater treatment. Demand for highly efficient adsorption materials intended for removal of environmentally unfriendly substances is growing worldwide. Preparing such an adsorbent from another industrial or agricultural waste seems to be a model

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concept. For example, bottom ash and de-oiled soya were employed for removal of hazardous dyes from wastewater [1–3]. Gupta et al. [4–6] used various agricultural industry waste, waste of thermal power plants and activated carbon developed from fertilizer waste for removal of some heavy metal ions from aqueous solutions. Such a waste can be blast furnace slag (BFS) which can be used for adsorptive removal of soluble phosphates from wastewater. Increased content of phosphate is a reason for eutrophication of surface water.

BFS is a complex system of stable composition made of major components such as $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ and some of minor importance. It was found that it characterized by relatively high sorption capacity for phosphorus which was proved by batch experiments [7, 8], column experiments [9] and also field research [10]. Retention of phosphates from aqueous solutions is carried out by various mechanisms. A dominant retention mechanism is often conditioned by a lot of factors such as structure of used sorbent, time of sorption or pH of solution [11]. In the case of BFSs, the dominant retention mechanism at $\text{pH} < 8$ is physical adsorption, while precipitation of Ca-phosphates dominates at $\text{pH} > 10$ [12].

The aim of the research was the improvement of adsorption properties of BFS. One of the methods is alkaline activation of BFS by hydrated lime [13]. The result of activation is a formation of new crystalline Ca-phases on the surface of the slag [14, 15] which leads to increase of its active surface and of content of available Ca(II). On the other hand, higher alkalinity of the sorbent and worse desorbability of captured phosphate is a negative aspect [15].

The work offers a new method which leads to substantial improving sorption abilities of BFS. The method is based on disintegration of the slag using high pressure of water and further controlled vacuum freezing of obtained suspension. The result is a sorbent with high active surface whose structure is close to nanocomposite material. Its characteristics were tested on phosphate sorption from aqueous solutions.

2. EXPERIMENTAL

Amorphous BFS was used as a starting material. It is a by-product of the steel manufacturing company Trinecke Železarny – Moravia Steel (Czech Republic). Granularity of the BFS was adjusted by crushing and sieving to obtain material below 0.1 mm in diameter. The chemical composition of BFS is shown in the Table 1.

Table 1

Composition of BFS [wt. %]

Sample	CaO	MgO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	MnO	K ₂ O
BFS	33.30	12.30	8.30	45.00	1.11	0.64	0.39

High pressure water jet mill cavitation disintegrator and controlled vacuum freeze dryer (patent no. CZ305704) were used for disintegration of BFS (BFS-D). Specific surface areas of both slag BFS and BFS-D were measured using the S^{BET} method on the machine Sorptomatic 1990, Thermofinnigan, Italy.

The mid-FTIR spectra were recorded using the ATR technique on an FTIR spectrometer (Nicolet NEXUS 470, ThermoScientific, USA) in the mid-IR region ($4000-400\text{ cm}^{-1}$) at room temperature with the resolution of 4 cm^{-1} and at 64 scans.

Adsorption tests on BFS and BFS-D were conducted through batch experiments. 0.5 g of sorbent was added into a 250 cm^3 flask containing 100 cm^3 of KH_2PO_4 solution. The phosphate concentration in tested solutions amounted to $100-1000\text{ mg PO}_4^{3-}\cdot\text{dm}^{-3}$. The suspensions were agitated in a horizontal shaking apparatus at the rate of 180 min^{-1} for 72 h, and then filtered. The volume of 100 cm^3 of a 5% water solution of Na_2CO_3 for the determination of the phosphate desorption degree was added to the filter cake. These suspensions were agitated in a horizontal shaking apparatus at the rate of 180 min^{-1} for 24 h, and then filtered. The residual phosphate contents expressed as phosphorus in all filtrates were determined spectrophotometrically as phosphorus-molybdenum blue using a UV spectrophotometer (UV-1800 Shimadzu, Japan). All chemicals used were of analytical grade.

Adsorption data were verified by the models of Freundlich and Langmuir isotherm. Linearized forms of both isotherms were used for evaluation. The Langmuir isotherm is determined as

$$Q_E = Q_m \frac{K_L c_E}{1 + K_L c_E} \quad (1)$$

While for the linearized Freundlich isotherm the following equation applies

$$\ln Q_E = \ln K_F + \beta \ln c_E \quad (2)$$

where Q_E ($\text{mg}\cdot\text{g}^{-1}$) is the equilibrium adsorption capacity, Q_m ($\text{mg}\cdot\text{g}^{-1}$) – maximum Langmuir adsorption capacity, c_E ($\text{mg}\cdot\text{dm}^{-3}$) – equilibrium concentration of adsorbate, K_L ($\text{dm}^3\cdot\text{mg}^{-1}$) – Langmuir constant, K_F – Freundlich constant ($\text{mg}\cdot\text{g}^{-1})(\text{mg}\cdot\text{dm}^{-3})^{-\beta}$, β – heterogeneity factor.

3. RESULTS AND DISCUSSION

Characterization of original and disintegrated BFS samples from the point of view of elements distribution was provided. The result is summed up in Fig. 1. Original amorphous BFS is a fine powder with an average particle size 1486 nm. By its disintegration,

BFS-D was obtained of average particle size of 198 nm. It is a material which is significantly close to nanocomposites according to its particle size.

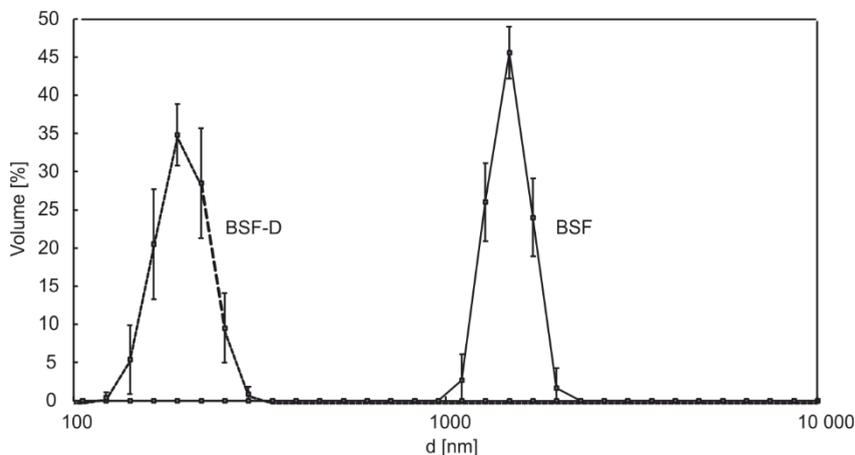


Fig. 1. Particle size distributions of BFS and BFS-D

Specific surface area of BFS-D sample was determined by the S^{BET} method and the obtained result was compared with that for the original slag (Fig. 2). It is obvious that after BFS disintegration, the specific surface area was increased 27-times. This significant increase should positively reflect in sorption abilities of the disintegrated material.

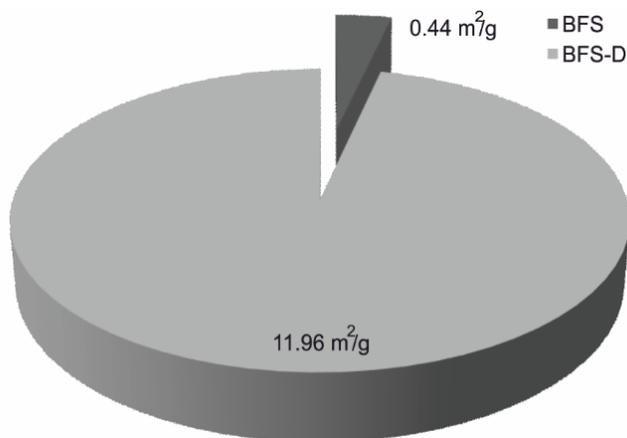


Fig. 2. Specific surface areas of original and disintegrated BFS

Therefore BFS-D sample was tested as a sorbent for phosphate removal from aqueous solutions. Obtained data were verified by the Freundlich and Langmuir adsorption models. The parameters of both sorption models are listed in Table 2.

Table 2

Data on phosphate adsorption on BFS and BFS-D

Components	Langmuir isotherm			Freundlich isotherm		
	q_m [mg P/g]	K_L [dm ³ /mg]	R^2	β	K_F [(mg·g ⁻¹)(mg·dm ⁻³) ^{-β}]	R^2
BFS	13.423	0.148	0.990	0.151	5.871	0.858
BFS-D	30.488	0.165	0.979	0.093	16.226	0.952

It is obvious that adsorption of phosphates on BFS-D can be characterized similarly as in the BFS case, using Langmuir isotherm. Basic retention mechanisms of phosphates (physical adsorption, surface complexation and Ca phosphates precipitation) do not change by disintegration of the slag. Linearized Langmuir isotherms for both slags show significant differences (Fig. 3).

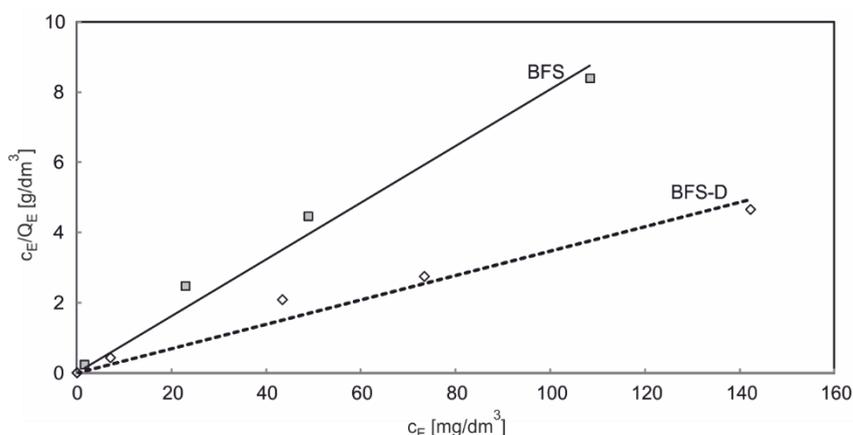


Fig. 3. The linearized Langmuir isotherm of phosphorus for BFS and BFS-D in the course of phosphate adsorption

Table 3

Characteristic properties of BFS and BFS-D

Adsorbents	Particle size [nm]	Specific surface area [m ² /g]	Q_m [mg P/g]
BFS	1486	0.44	13.42
BFS-D	198	11.96	30.49

The maximum adsorption capacity of BFS-D was 30.49 mg P/g, which corresponds to a 127% increase with respect to that of BSD. Moreover, the β values in Table 2 indicate that the adsorption of phosphates on BFS-D due to fairly smaller texture and bigger

specific surface area is more homogenous than that on BFS. Comparison of the characteristic properties of the both adsorbents is summarized in Table 3.

For detailed explanation of BFS-D structure and adsorption mechanisms, FTIR spectra of original BFS, BFS-D and BFS-D after phosphate adsorption were recorded (Fig. 4). For BFS (curve a) and BFS-D (curve b) dominant broad peak is typical of the band of 850–1020 cm^{-1} which corresponds to bond vibrations Si–O in SiO_4 tetrahedrons and bond vibrations of Si–O–Al in aluminum silicates [16, 17]. A smaller distinct peak at 510 cm^{-1} can be attributed to O–Si–O bonds in silicates [17].

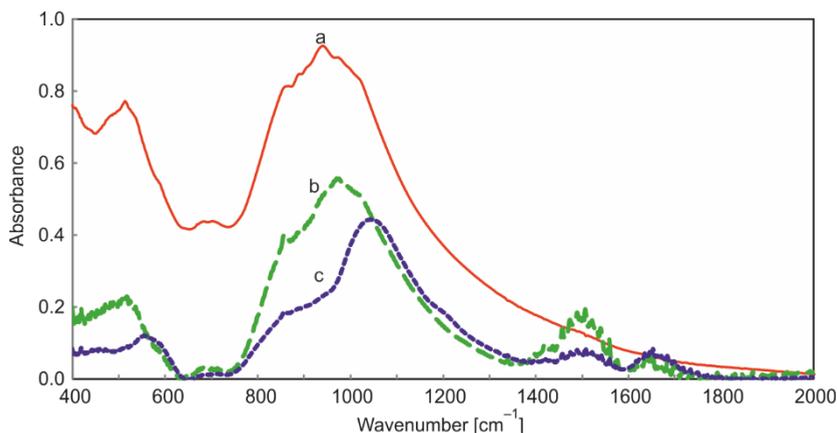


Fig. 4. FTIR spectra of BFS (a), BFS-D (b) and BFS-D after phosphate adsorption (c)

From FTIR-records (a) and (b) in Fig. 4, it is obvious that both peaks lie at the same frequencies, however, their intensities differ. Significant decrease of peak intensity for BFS-D (b) can be explained by partial destruction of bonds. Disintegration process which leads to formation of material similar to nanocomposites causes changes in quantity of bonds in silicates and aluminosilicates. A part of these bonds decomposes by BFS disintegration.

On FTIR of BFS-D after adsorption of phosphate (c) dominant peak at 1043 cm^{-1} is apparent, which covers original broad peak of silicates and aluminosilicates. The peak can be attributed to calcium phosphates precipitated in a hydroxyapatite (HAp) form [18]. Also a smaller peak at 553 cm^{-1} corresponds to vibration of O–P–O bonds in phosphates [19], which appears in low frequency band. The lower intensity of spectrum (c) shows surface precipitation of phosphates. The peaks at 1650 and 1500 cm^{-1} in spectra (b) and (c) correspond to molecule-bound H_2O and CO_3 groups in carbonates [20]. Water as well as CO_2 in a form of carbonates entered into BFS-D during the disintegration process.

The results show that surface precipitation of HAp seems to become a main mechanism of phosphate retention from aqueous solutions in BFS-D. The reason is bigger

specific surface area of BFS-D and primarily better accessibility of surface-active Ca(II) compared to BFS. This knowledge is also supported by results of desorption tests. Desorption tests performed according to [15, 21] were aimed to assess the availability of captured phosphorus. It was found that the desorption efficiency D of phosphates from BFS amounted 89.98%, while that of BFS-D only 34.62%. It is evident that the formation of the HAp phase on the BFS-D is caused by low availability of the phosphate and results in low desorption efficiency.

4. CONCLUSIONS

In the paper, a new disintegration method has been presented, which leads to a significant improvement of the adsorption ability of blast furnace slag (BFS). A high pressure water jet mill cavitation disintegrator and controlled vacuum freeze dryer were used for disintegration of amorphous BFS. As a result, the adsorbent with high sorption surface area was obtained. This modified material (BFS-D) is similar to nanocomposites and has 27-times larger free surface area than original BFS. Average particle size is 198 nm. The adsorption properties of BFS-D were tested for phosphate removal from aqueous solutions. The adsorption capacity of BFS-D increased by 127% compared to original non-modified slag and amounted to 30.49 mg P/g. Due to better accessibility of surface-active Ca(II), the precipitation of hydroxyapatite becomes a dominant retention mechanism. It leads to worse desorption of phosphorus in alkaline environment. On the other hand, hydroxyapatite can represent available form of phosphorus for acid environment.

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REFERENCES

- [1] MITTAL A., KAUR D., MALVIYA A., MITTAL J., GUPTA V.K., *Adsorption studies on the removal of coloring agent phenol red from wastewater using waste materials as adsorbents*, J. Colloid Interface Sci., 2009, 337, 345.
- [2] MITTAL A., MITTAL J., MALVIYA A., GUPTA V.K., *Adsorptive removal of hazardous anionic dye Congo Red from wastewater using waste materials and recovery by desorption*, J. Colloid Interface Sci., 2009, 340, 16.
- [3] MITTAL A., MITTAL J., MALVIYA A., GUPTA V.K., *Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials*, J. Colloid Interface Sci., 2010, 344, 497.
- [4] GUPTA V.K., IMRAN A., *Removal of lead and chromium from wastewater using bagasse fly ash-a sugar industry waste*, J. Colloid Interface Sci., 2004, 27, 21.

- [5] GUPTA V.K., NAYAK A., *Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe₂O₃ nanoparticles*, Chem. Eng. J., 2012, 180, 81.
- [6] GUPTA V.K., SRIVASTAVA S.K., MOHAN D., SHARMA S., *Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions*, Waste Manage., 1997, 17, 517.
- [7] OGUZ E., *Removal of phosphate from aqueous solution with blast furnace slag*, J. Hazard. Mater. B, 2004, 114, 131.
- [8] KOSTURA B., KULVEITOVÁ H., LEŠKO J., *Blast furnace slags as sorbents of phosphate from water solutions*, Water Res., 2005, 39, 1795.
- [9] JOHANSSON L., *Blast furnace slag as phosphorus sorbents – column studies*, Sci. Total Environ., 1999, 229, 89.
- [10] JOHANSSON L., GUSTAFSSON P., *Phosphate removal using blast furnace slags and opoka-mechanisms*, Water Res., 2000, 34, 259.
- [11] YANG J., WANG S., LU Z., LOU S., *Converter slag-coal cinder columns for the removal of phosphorous and other pollutants*, J. Hazard. Mater., 2009, 168, 331.
- [12] BHATNAGAR A., SILLANPÄÄ M., *Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment. A review*, Chem. Eng. J., 2010, 157, 277.
- [13] GONG G., YE S., TIAN Y., WANG Q., NI J., CHEN Y., *Preparation of a new sorbent with hydrated lime and blast furnace slag for phosphorus removal from aqueous solution*, J. Hazard. Mater., 2009, 166, 714.
- [14] ROY A., SCHILLING P.J., EATON H.C., BRABSTON W.N., WAKELEY L.D., *Activation of ground blast-furnace lag by alkali-metal and alkaline-earth hydroxides*, J. Am. Ceram. Soc., 1992, 75, 3233.
- [15] KOHUTOVÁ H., KOSTURA B., KUKUTSCHOVÁ J., MATÝSEK D., *Oxyhumolite influence on adsorption and desorption of phosphate on blast furnace slag in the process of two-stage selective adsorption of Cu(II) and phosphate*, Chem. Pap., 2014, 68, 766.
- [16] MARTÍNEZ-ZAPATA O., MÉNDEZ-VIVAR J., BOSCH P., LARA V.H., *Synthesis and characterization of amorphous aluminosilicates prepared by sol-gel to encapsulate organic dyes*, J. Non-Cryst. Solids, 2011, 357, 3480.
- [17] SÁEZ DEL BOSQUE I.F., MARTÍNEZ-RAMÍREZ S., BLANCO-VARELA M.T., *FTIR study of the effect of temperature and nanosilica on the nano structure of C–S–H gel formed by hydrating tricalcium silicate*, Constr. Build. Mater., 2014, 52, 314.
- [18] MAITZ M.F., PHAM M.T., MATZ W., REUTHER H., STEINER G., *Promoted calcium-phosphate precipitation from solution on titanium for improved biocompatibility by ion implantation*, Surf. Coat. Technol., 2002, 158, 151.
- [19] SZUMERA M., *Structural investigations of silicate-phosphate glasses containing MoO₃ by FTIR, Raman and ³¹P MAS NMR spectroscopies*, Spectrochim. Acta Part A, 2014, 130, 1.
- [20] MOSTAFA N.Y., KISHAR E.A., ABO-EL-ENEIN A.A., *FTIR study and cation exchange capacity of Fe³⁺ and Mg²⁺ substituted calcium silicate hydrates*, J. Alloys Compd., 2009, 473, 538.
- [21] KOSTURA B., MATÝSEK D., KUKUTSCHOVÁ J., LEŠKO J., *Phosphate interaction with calcined form of Mg-Al-CO₃ hydrotalcite in aqueous solutions*, Ann. Chim., 2012, 37 (1), 11.