

THE CHANGE IN SURFACE AREA PROPERTIES OF BLAST FURNACE SLUDGE TREATED BY CITRIC ACID

A. Rađenović^{1*} - J. Malina¹ - G. Matijašić²

¹Faculty of Metallurgy, University of Zagreb, Aleja narodnih heroja 3, 44 000 Sisak

²Faculty of Chemical Engineering and Technology, Marulićev trg 19, 10 000 Zagreb

ARTICLE INFO

Article history:

Received 18.07.2012.

Received in revised form 06.12.2012.

Accepted 06.12.2012.

Keywords:

Blast furnace sludge

Waste material

Chemical and heat treatment

Surface area properties

Abstract:

The blast furnace sludge (BFS) is a waste material of pig iron production. The chemical and mineralogical composition of BFS was examined by Proton Induced X-ray Emission (PIXE) and X-ray Diffraction (XRD) methods. Surface area properties (specific surface area, average pore diameter, total pore volume) are determined by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method. The microscopic observation was conducted using a scanning electron microscopy (SEM method).

Chemical treatment of BFS was performed by adsorbed citric acid. Thermal treatment was done by heating at 700°C. The surface properties of the blast furnace sludge are compared to those obtained after treatment. The results have shown that this successfully performed experiment modified the surface of BFS as a potentially low-cost adsorbent.

1 Introduction

The area is a fundamentally important feature of the adsorbents. Adsorption is one of the most popular methods for the removal of inorganic and organic matter from the aqueous solutions. It is a surface phenomenon, in which molecules of adsorbate are attracted and held on the surface of an adsorbent until an equilibrium has been reached between adsorbed molecules and those still freely distributed in the bulk of the gas or liquid.

The adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species.

Activated carbons are unique and versatile adsorbents because of the availability of extensive

surface area, its porous structure and high adsorption capacity. Basically, there are two different processes for the preparation of activated carbon: the physical and chemical activation. The physical activation involves carbonization of a carbonaceous precursor followed by gasification of the resulting char in the presence of some oxidizing gases or direct activation of the starting material in the presence of an activating agent (such CO₂, steam, N₂, H₂, O₂) [1, 2]. On the other hand, in chemical activation the precursor is impregnated with certain chemicals such as KOH, K₂CO₃, NaOH, ZnCl₂, H₃PO₄, and H₂SO₄ and, afterwards, is pyrolyzed [3-5]. The advantages of chemical activation are lower temperatures of the process (500-700°C) than those needed for physical

* Corresponding author. Tel.: 044 533379;

fax: 044 533378

E-mail address: radenova@simet.hr

activation (800-1100°C) and high product yields. The high cost of activated carbon restricts their use. Hence, the less expensive non-conventional adsorbents are being studied including their surface modification [6-9]. This can be performed by adsorbing specific organic compounds on the surface of carbons.

Currently, there are many studies on the development of low-cost adsorbents using industrial by-products and waste materials for the removal of mainly heavy metals and dyes from aqueous solutions [10-12].

Blast furnace sludge (BFS) is a by-product of the steelmaking industry. The gases generated during the manufacture of pig iron carry a dust load which is cleaned before their release in the atmosphere. The coarse particles in the exhaust gases are removed by passing the gases through a large lined chamber. The velocity of gases is reduced to allow the settling of dust load and the waste material is collected as blast-furnace dust. The finer particles, which remain in the gas, are removed in wet scrubbers; the waste material collected here is BFS. The aim of this work is to investigate the influence of chemical treatment with citric acid (CA) and thermal treatment by heating at 700°C, and the change in surface area properties of the blast furnace sludge.

2 Experimental

2.1 Samples

The sample of original BFS, provided by a Croatian Iron & Steelmaking Company, was dried at 105 °C for 4 hours to yield a powder of a particle diameter less than 100 µm.

The chemical composition of the ground sample was determined by Proton Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS) techniques. PIXE quantification was done using GUPIX, and RBS determinations used SIMNRA software [13].

Conventional X-ray diffraction (XRD) analysis yields a qualitative mineralogical composition. The accurate quantitative composition of BFS is achieved by Rietveld refinement of XRD analyses [14]. In this work ZnO was used as the internal standard. ZnO was mixed with the samples to give a proportion of $w = 10\%$. The mineralogical composition of these mixtures was determined by

XRD analysis using a Philips PW 1710 diffractometer with Cu K_{α} radiation.

2.2 Chemical and heat treatment

Chemical treatment was performed using citric acid adsorption on the BFS. Citric acid is tricarboxylic acid ($\text{HOOC-CH}_2\text{-COH-COOH-CH}_2\text{-COOH}$). The results of the citric acid adsorption on the BFS were published earlier [15]. Heat treatment was done by heating BFS at 700°C in a muffle furnace until a constant mass was obtained.

2.3 Analysis of surface area properties

The surface area properties were determined by the Brunauer-Emmett-Teller (BET) method. The N_2 adsorption-desorption isotherms of the investigated samples were measured using a Micromeritics ASAP 2000 adsorption instrument in order to determine the surface area and total pore volume. The average pore diameter is calculated using the equation:

$$d = \frac{4 \cdot V_p}{S_p}, \quad (1)$$

where V_p is a specific volume and S_p is a specific surface area. Pore size distribution of BFS is calculated by the Barrett-Joyner-Halenda (BJH) method [15]. Before the conducting an analysis, the BFS samples were heated at a temperature of 50°C and evacuated under $666.5 \cdot 10^{-3}$ Pa pressure in order to remove any contaminants as well as moisture that might be present on the surface.

2.4 Examination of surface morphology

The surface morphology of BFS samples was examined by the method of qualitative scanning electron microscopy (SEM) using Jeol JXA 50A microscope.

3 Results and discussion

The chemical composition of BFS is shown in Table 1. The results of chemical analyses have shown that BFS is dominated by O (42.23 %) and C (31.74 %). Then follow Si (6 %), Zn (4.52 %), Na (3 %), Al (3 %) etc. The mineralogical inventory

revealed that BFS is dominated by an amorphous phase (76.2 %, Table 2) composed mainly of coke and a less crystalline oxides or hydroxides of metals such as Al, Pb, Zn, Fe as described by Mansfeldt and Dohrmann [16].

Besides elemental iron (α -Fe), BFS is composed mainly of calcite CaCO_3 , magnetite Fe_3O_4 , kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and smithsonite ZnCO_3 . Such a composition of BFS can be explained by processing conditions of the pig iron production in the blast-furnace process. While fluxing agents are the source of both calcite and dolomite, quartz and kaolinite originate mainly from ash-containing coke; iron ores are the source of magnetite and hematite. Some C originates from carbonates (Table 1) that are components of the carbonaceous flux. However, coke-bonded C is the main source of carbon in the BFS. Literature data [17] indicate that the BFS with such composition could be considered as an effective adsorbent. This can be related to its high

oxides and carbon mass fraction since both contain oxygenated surface functional groups.

A fundamentally significant feature of adsorbents is their high porosity and usually a high surface area. That is why their most important characteristics deal with total pore volumes, pore size distribution over the pore diameter and the specific surface area. Adsorption capacities can be related to the surface area properties of BFS as follows.

Table 3 presents the results of the surface area properties of BFS: the specific surface area, average pore diameter, total pore volume (1.7-300 nm) before and after treatment. The value of BET surface area for BFS before treatment is $S_p = 31.46 \text{ m}^2/\text{g}$. This surface area could be explained by the fine – grained particle size of BFS and their porous nature. Total pore volume was calculated at the relative pressure close to saturation in the adsorption branch yielding $V_p = 157 \cdot 10^{-3} \text{ cm}^3/\text{g}$. The average pore diameter, $d = 17.88 \text{ nm}$ was calculated

Table 1. Chemical composition of blast furnace sludge.

CHEMICAL COMPOSITION, wt %			
Element			
O	42.23	Pb	0.99
C	31.74	K	0.66
Si	6.00	Mn	0.66
Zn	4.52	S	0.62
Na	3.00	P	0.14
Al	3.00	Cl	0.05
Fe	2.90	Ti	0.05
Ca	2.30	Cu	0.01
Mg	1.00		

Table 2. Mineralogical composition of blast furnace sludge.

MINERALOGICAL COMPOSITION, wt %		
Phase	Formula	
x-ray amorphous		76.2
calcite	CaCO_3	9.9
magnetite	Fe_3O_4	6.3
kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	2.1
smithsonite	ZnCO_3	2.1
dolomite	$\text{Ca,Mg}(\text{CO}_3)_2$	1.6
α -quartz	$\alpha\text{-SiO}_2$	1.1
α -hematite	$\alpha\text{-Fe}_2\text{O}_3$	0.4
α -elemental iron	$\alpha\text{-Fe}$	0.2

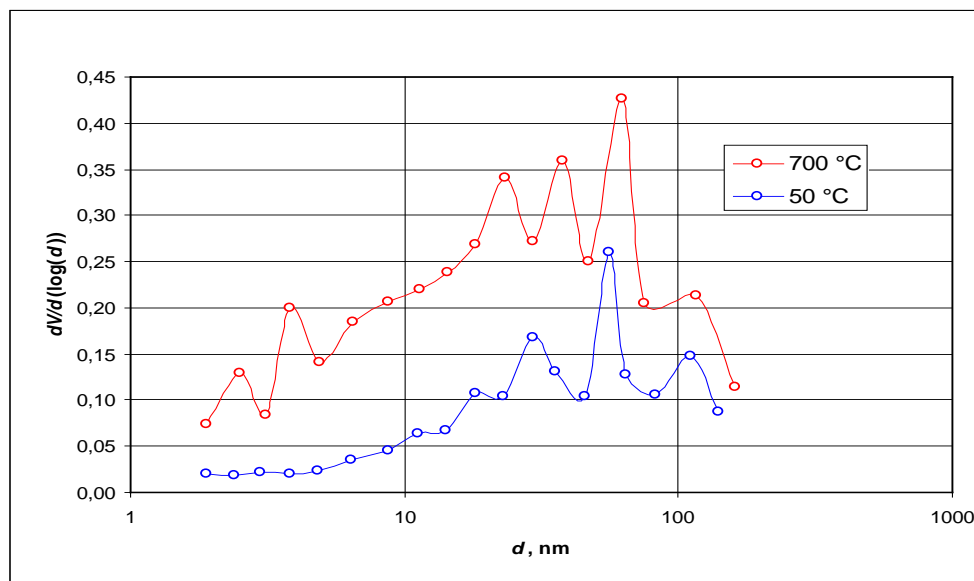


Figure 1. Pore size distribution of BFS previously degassed at 50°C and afterwards heated at 700°C.

using the equation (1).

According to the IUPAC classification, the pores of porous material are classified into three groups: micropores (width $d < 2$ nm), mesopores ($2 \text{ nm} < d < 50$ nm) and macropores ($d > 50$ nm) [1]. Hence, BFS may be considered a mesoporous material.

Pore size distribution of BFS degassed at 50°C is shown in Fig. 1. The fraction of pore size between 10 and 100 nm is presented in the greatest proportion. The heating of the same sample at 700°C leads to significant changes in investigated properties. The proportion of smaller pores increased, which results in almost four times higher specific surface area ($S_p = 121.93 \text{ m}^2/\text{g}$, Table 3) compared to the untreated sample (BFS+50°C, Table 3). The average pore diameter is decreased from 17.88 to 12.94 nm.

After chemical treatment of BFS with CA (sample BFS+CA, 50°C), investigated surface properties are considerably different. BET surface area of BFS has a very low value ($S_p = 3.31 \text{ m}^2/\text{g}$). The sample was nearly non-porous (Fig. 2). The average pore diameter of chemically treated BFS is decreased to 3.21 nm in relation to the value of 17.88 nm for BFS before treatment. The values of the total pore volume (1.7-300 nm) of chemically treated BFS ($V_p = 157 \cdot 10^{-3} \text{ cm}^3/\text{g}$) are considerably lower than the total pore volume of untreated BFS ($V_p = 2.4 \cdot 10^{-3} \text{ cm}^3/\text{g}$).

The BET surface area of a chemically treated sample and subsequently heat treated at 700°C

(sample BFS+CA, 700°C) is multiply higher ($S_p = 84.49 \text{ m}^2/\text{g}$, Table 3) than those for only chemically treated sample ($S_p = 3.31 \text{ m}^2/\text{g}$). The average pore diameter of this sample is increased to 9.74 nm in relation to the same parameter for sample before heating at 700°C ($d = 3.21$ nm). Likewise, the value of the total pore volume (1.7-300 nm) is increased and amounts to $226 \cdot 10^{-3} \text{ cm}^3/\text{g}$.

These results were confirmed by the surface morphology investigations. Fig. 3 shows the SEM image of the blast furnace sludge sample before chemical treatment. Some heterogeneities and pores of different size (Fig. 3a) are visible. The BFS contains a complex porous structure, which consists of pores of different sizes and shapes. The scanning electron microscopy enables the direct observation of any surface morphology changes in the BFS due to the acid adsorption. After chemical treatment, accumulations and deposits of CA (Fig. 3b) adsorbed on BFS surface are clearly visible. A different pore diameter is also observed as change in morphology of samples.

The change in pore size distribution yield to enhancement of the specific surface area of a heat treated BFS sample. Besides, significant mass loss of 32 % contributes to the change in the porous structure of BFS. Mass loss is caused by partial thermal decomposition and separation of some compounds from the BFS, such as physical and chemical moisture, sulphates and carbonates [18]. A large mass fraction of the amorphous phase has also

a beneficial effect on the development and pore distribution or the specific surface area.

It seems that reason for it is a partial availability of pores in adsorption of CA molecules on the surface. The comparison of obtained results shows better parameters of BFS surface properties after heat treatment of the chemically treated sample than after only the chemically treated ones with CA. Regardless of that, the chemically treated sample with CA could become more active binding of adsorbates (like metallic ions) via complexes formed onto acid modified surface. According to literature data, adsorption capacity of adsorbents

increases after treatment with acids; so less active adsorbents can be used.

The surface properties of adsorbents are influenced to a great extent by foreign elements fixed on the surface, in particular by oxygen, through functional groups responsible for the reactivity of the surface [19].

In this work, citric acid is utilized as biodegradable and widely used low cost acid in the food and pharmaceutical industries. Similar investigations by applying other acids (tartaric acid, fulvic acid, acetic acid) were conducted previously [6, 20, 21].

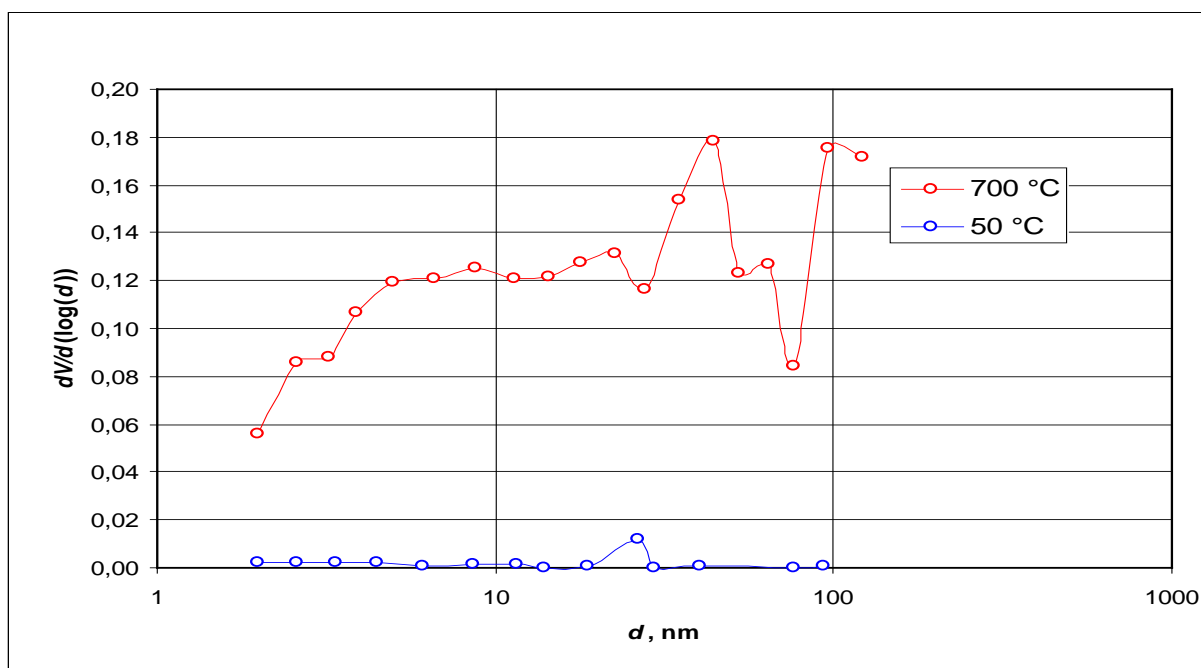


Figure 2. Pore size distribution of BFS treated with citric acid, previously degassed at 50°C and afterwards heated at 700°C.

Table 3. Results of investigation of BFS surface properties.

SAMPLE	PROPERTIES		
	Specific surface area, $S_{BET}, m^2/g$	Total pore volume (1,7-300 nm), $V_p \cdot 10^3, cm^3/g$	Average pore diameter, d, nm
BFS(50°C)	31.46	157	17.88
BFS (700°C)	121.93	420	12.94
BFS+CA (50°C)	3.31	2.4	3.21
BFS+CA (700°C)	84.49	226	9.74

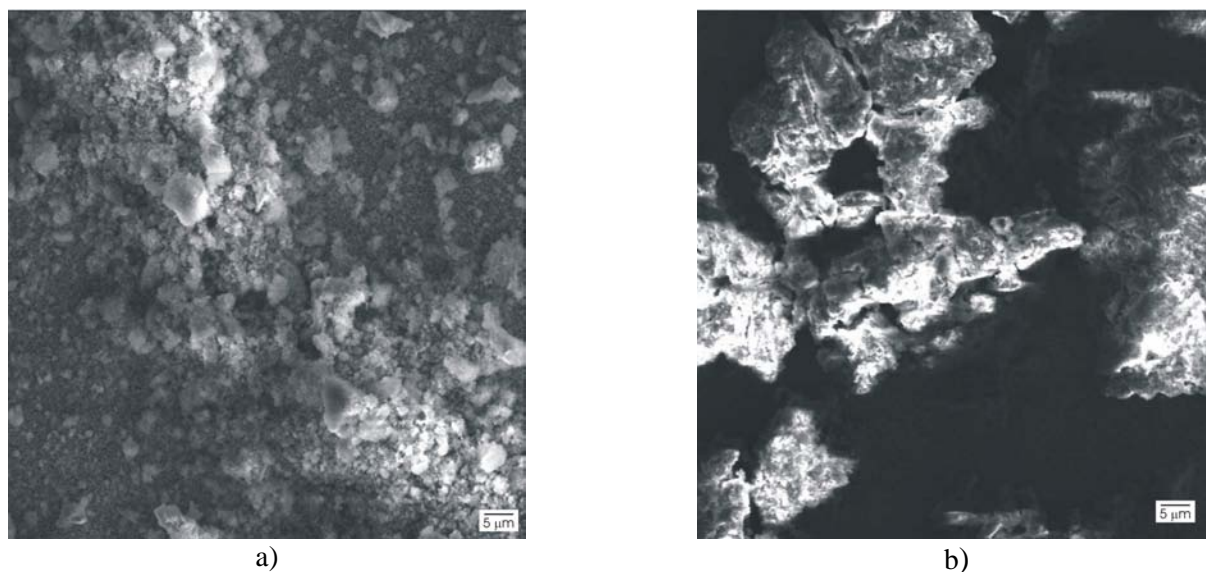


Figure 3. SEM micrographs of BFS surface: a) before treatment with citric acid; b) after treatment with citric acid (concentration of 0,05 mol/L, contact time 24 hours).

4 Conclusion

The examined chemical composition of blast furnace sludge has shown a high content of carbon. The mineralogical inventory revealed that BFS is dominated by an amorphous phase and consists mainly of oxides and carbonates. The surface properties of the blast furnace sludge have been compared to those obtained after the treatment. The both chemical treatment of BFS by citric acid and heat treatment to 700°C have changed their surface area properties and surface morphology. Reducing of pore size and better pore size distribution of BFS are the result of applied activation procedure. The results have shown that experiment performed successfully modified the surface of BFS. The comparison of obtained results shows better parameters of BFS surface properties after heat treatment chemically treated samples than the ones being only chemically treated with CA.

Owing to their chemical and surface properties, BFS could be used as a porous adsorbent. For more complete evaluation of BFS adsorption capability, the surface chemistry determination is recommended.

References

- [1] Hu, Z., Srinivasan, M. P., Yaming, N.: *Novel activation process for preparing highly microporous and mesoporous activated carbons*, Carbon, 39 (2001), 6, 877-886.
- [2] Ahmedna, M., Marshall, W. E., Rao, R. M.: *Surface properties of granular activated carbon from agricultural by-products and their effects on raw sugar decolorization*, Bioresource Technology, 71 (2000), 2, 103-112.
- [3] Ozer, A. Pirincci, H. B.: *The adsorption of Cd(II) ions on sulphuric acid-treated wheat bran*, Journal of Hazardous Materials, 137 (2006), 2, 849-855.
- [4] Puziy, A. M., Poddubnaya, O.I., Martinez-Alonso, A. Suarez-Garcia, F., Tascon, J. M. D.: *Synthetic carbons activated with phosphoric acid. I. Surface chemistry and ion binding properties*, Carbon, 40 (2002), 13, 1493-1505.
- [5] Rađenović, A., Štrkalj, A., Malina, J.: *Properties of the chemically activated carbon anode dust*, Engineering Review, 29 (2009), 1, 13-20.
- [6] Rađenović, A., Malina, J.: *Adsorption ability of the carbon black for nickel ions uptake from aqueous solution*, Hemijska Industrija /Chemical Industry, 67 (2013), in press.
- [7] Rađenović, A., Malina, J., Slokar, J.: *Carbon black surface modification by organic acids*,

- Proceedings of the 2nd Croatian Congress on Microscopy, Hrvatsko društvo za elektronsku mikroskopiju, Zagreb, Croatia, 2006, 262-264.
- [8] Marshall, W. E., Akin, D. E., Wartelle, L. H., Annis, P. A.: *Citric acid treatment of flax, cotton and blended nonwoven mats for copper ion adsorption*, Industrial Crops and Products, 26 (2007), 1, 8–13.
- [9] Jiuhui, Q. U.: *Research progress of novel adsorption processes in water purification: A review*, Journal of Environmental Sciences, 20 (2008), 1, 1–13.
- [10] Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Rivera-Utrilla, J., Sanchez-Polo, M.: *Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review*, Journal of Environmental Management, 85 (2007), 4, 833–846.
- [11] Barakat, M. A.: *New trends in removing heavy metals from industrial wastewater*, Arabian Journal of Chemistry, 4 (2011), 4, 361-377.
- [12] Babel, S., Kurniawan T. A.: *Low-cost adsorbents for heavy metals uptake from contaminated water: a review*, Journal of Hazardous Materials, 97 (2003), 1-3, 219–243.
- [13] Bogovac, M., Bogdanovic, I., Fazinić, S., Jakšić, M., Kukec, L., Wilhelm, W.: *Data acquisition and scan control system for nuclear microprobe and other multiparameter experiments*, Nuclear Instruments and Methods, 89 (1994), 1-4, 219-222.
- [14] Young, R. A.: *The Rietveld Method*, Oxford University Press, Oxford, 1993.
- [15] Rađenović, A., Malina, J.: *Adsorption of organic acids on blast furnace sludge*, Chemical and Biochemical Engineering Quarterly, 23 (2009), 2, 187-193.
- [16] Mansfeldt, T., Dohrmann, R.: *Chemical and mineralogical characterization of blast-furnace sludge from an abandoned landfill*, Environmental Science and Technology, 38 (2004), 22, 5977-5984.
- [17] López-Delgado, A., Pérez, C., López, F. A.: *The influence of carbon content of blast furnace sludge and coke on the adsorption of lead ions from aqueous solution*, Carbon, 34 (1996), 3, 423-426.
- [18] Dean, J. A.: *Lange's Handbook of Chemistry*, Mc Graw-Hill Book Company, New York, 1985.
- [19] Boehm, H. P.: *Some aspects of the surface chemistry of carbon blacks and other carbons*, Carbon, 32 (1994), 5, 759-769.
- [20] Du, Q., Sun, Z., Forsling, W., Tang, H.: *Complexations in illite-fulvic acid-Cu²⁺ systems*, Water Research (1999), 3, 693-706.
- [21] Wong, K. K., Lee, C. K., Low, K. S., Haron, M. J.: *Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk*, Process Biochemistry, 39 (2003), 4, 437-445.

