Carbonaceous Materials from Rice Husk: Production and Application in Industry and Agriculture

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Abstract

A solid carbonaceous material and a liquid product were produced by the rice husk pyrolysis. Chemical analysis and GC-MS were used to investigate the compositions of the prepared materials, respectively. X-ray, SEM, TEM, BET were applied to study the structure and textural properties of the carbonaceous material. It was determined that the solid product is a composite consisting of carbon (52%) and silicon dioxide (31%) nanoparticles. Therefore, it was named a silicon-carbon. The liquid product is a water solution containing various organic compounds (carboxylic acids, phenols, ketones, alcohols and ethers, cyclic aliphatic hydrocarbons, heterocyclic compounds). The possibility to apply the solid carbonaceous material as a reducing agent and a sorbent and the liquid organic product as a flotation reagent was determined in the electro thermal smelting process, sorption and flotation processes. Veterinary and toxicology studies were performed to estimate toxicity of solid carbonaceous material and possibility to apply it as a feed additive. It was shown, that due to its chemical composition the silicon-carbon is a complex raw material for metallurgical silicon, aluminum-free and titanium-free ferrosilicium, and silicon carbide production. The produced sorbent had high rare and heavy metals adsorption capacity. The solid carbonaceous material, that was found to be non-toxic, was an effective feed additive and improved quality of laying hens and broiler chickens. The liquid product had properties of a blowing agent in the flotation of lead-zinc ores. It was concluded that both rice husk derived solid and liquid carbonaceous materials are economically effective alternative materials for various technological processes and agriculture.

Keywords: rice husk, pyrolysis, silicon-carbon, organic product, metallurgy, agriculture

Introduction

Large amounts of rice husk are generated over the world as a by-product of rice milling. Rice processing plants of Kazakhstan annually accumulate about 100 thousand tons of rice husks that up to now do not find industrial application and are sent to dumps. This, first of all, requires the rejection and removal from the national economic turnover of more and more areas of land, as it is not subject to decay, and secondly, it creates an unfavorable ecological situation. For this reason, a task to find an effective way of processing rice husk is very acute for Kazakhstan as well as other countries cultivating rice [Wang et al., 2010, Singh et al., 2002].

Most studies deal with producing adsorbents from rice husk because it is renewable environmentally friendly raw material [Chen et al., 2011, Sharma et al., 2013, Sukharnikov et al., 2007, Li et al., 2015, Srivastava et al., 2008]. However, there is no common method to prepare the adsorbent. There are few reasons for it. One is a difference in compositions of rice husk from different geographic regions. Therefore, it is necessary to study all kinds of rice husk in order to find the best processing way. Unfortunately, there is no enough information and research data on production of silicon containing materials [Singh et al., 2002] and feed additive [Lu et al., 2011, Baryshnikov, 2000,

Tab. 1. Chemical and elemental composition of silicon-carbon SC-400

Tab. 1. Skład chemiczny i pierwiastkowy krzemo-węgla SC-400

Moisture, %	Content, % mass.													
	SiO_2	Ca	Mg	K_2O	Na_2O	Fe	Ti	Al	Mn	Cu	C	H	N	$O_{org.}$
3.4	31.5	0.6	0.1	0.22	0.004	0.4	0.01	0.15	0.03	0.001	52.0	3.5	1.1	6.8

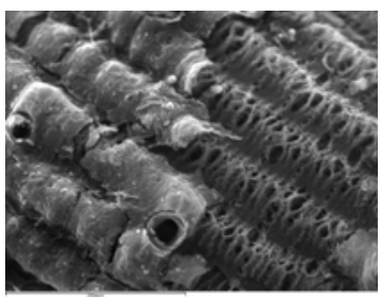

Fig. 1. Scanning electron micrograph of silicon-carbon SC-400

Rys. 1. Mikrografie SEM krzemo-węgla SC-400

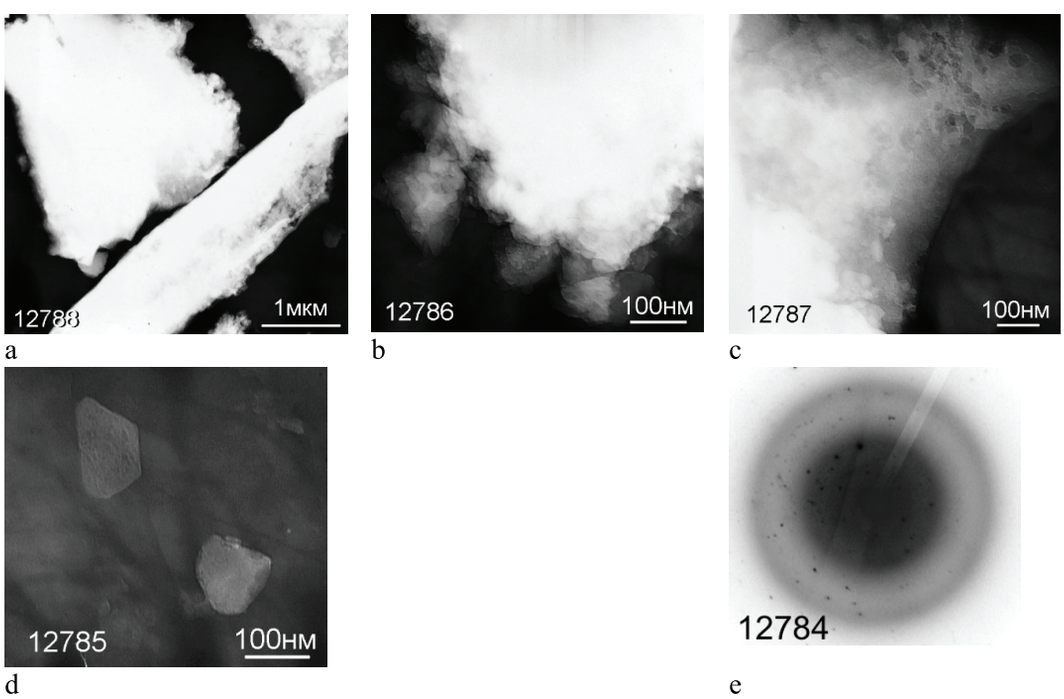

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Fig. 2. TEM images and diffraction pattern of silicon-carbon SC-400

Rys. 2. Zdjęcia TEM oraz obraz dyfrakcyjny krzemo-węgla SC-400

Patent CN102488101, 2011, Patent KR9400957-A, KR9400957-B1, 1994]. At the moment, there is no any reasonable solution for complex processing of rice husk.

We have developed a complex technology of thermal recycling of rice waste and created an equipment with output on rice husk of 300 kg per day [Efremova, 2012]. In this study we describe composition and structure of the prepared products and their treatment ways to use them in different fields of industry and agriculture.

Materials and methods

Rice husk (RH), obtained from an agricultural enterprise in Kyzylorda region, consisted of (wt.%, dry basis): cellulose (32.8), hemicellulose (17.2), lignin (25.5), extractives soluble in alcohol-benzene mixture (1.8) and hot water (6.2), silicon dioxide (15.5%), and other mineral substances (Na – 0.039; K – 0.355; Ca – 0.05; Mg – 0.065; Fe – 0.034; Al - <0.1). Rice husk was used as a precursor for the production of carbonaceous materials.

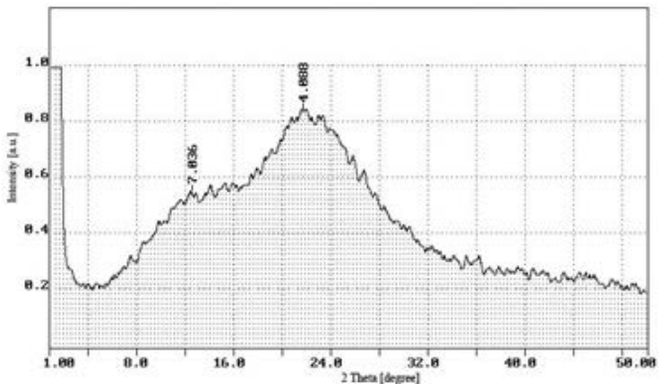

Fig. 3. XRD curve of silicon-carbon SC-400

Rys. 3. Analiza XRD krzemo-węgla SC-400

Tab. 2. Chemical compositions of silicon-carbon samples

Tab. 2. Skład chemiczny próbek krzemo-węgla

Sample	SiO_2	C	Ca	Fe	Al	P
SC-1	50.4	48.2	0.56	0.4	<0.15	<0.15
SC-2	76.5	22.1	0.95	0.55	<0.15	<0.15

Rice husk pyrolysis was carried out using a pilot set up for processing of 300 kg of rice husk per day. Plant raw material was heated in a rotary furnace at 400°C under off-gas atmosphere for 30 min. A steam-gas mixture was trapped and condensed to produce a liquid product. A solid product was cooled without air to room temperature and subjected to different ways of treatment for testing in metallurgical and sorption processes and agriculture.

The X-ray diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM) were applied to study the phase composition, macro- and microstructure of carbonaceous materials as it is described in [Yefremova et al., 2013].

The textural properties of the carbonaceous samples were measured using nitrogen isothermal adsorption-desorption method. The nitrogen adsorption-desorption isotherms were taken at -196°C using NOVA 2200 Surface Area and Pore Size Analyzer (Quantohrome, USA). The porous properties were determined using a model developed by Brunauer, Emmett and Teller, the Density Functional Theory (DFT), and the Barrett-Joyner-Halenda (BJH) methods.

Gas phase chromatography mass spectrometry (GC-MS) was applied to identify chemical content of the liquid product. GC-MS was performed on Agilent 6890 chromatograph with a mass selective detector.

Results

Solid carbonaceous product characteristics

As can be seen from the Table 1 rice husk pyrolysis solid product consists mainly of silica (31.5%) and carbon (52%). Due to this fact it was named as silicon-carbon (SC-400).

The silicon-carbon surface morphology is illustrated in Fig. 1. The SEM image shows that SC-400 as well as raw rice husk has a corrugated relief because silica is situated in the outer layer of rice husk and protects it from damage [Markovska, Lyubchev, 2007]. There are gaps that have appeared as a result of trichomes destruction on the outer epidermis. A pore structure formed probably by cellulose fibrous species under outer layer can be observed.

According to the results of transmission electron microscopy, SC-400 consists of the particles of different morphology and size. There are big plate-like and tubular particles, agglomerated formations consist of disperse round particles (20–50 nm) as well as particles having a pore surface (Fig. 2a–c). However, these pores could be formed during TEM investigation as a result of evaporation of some substances by the electron beam as it was observed in [Kiang et al., 1996]. Analysis of carbon phase diffraction patterns allows us to conclude that it is mainly amorphous. When we tested earlier silicon-carbon produced at 600°C [Yefremova et al., 2013] we observed diffraction rings indexed with the d(002) of carbon that was calculated to be 0.346–0.372 nm. There are some particles with a geometrically regular shape (Fig. 2d). Apparently, these particles are microcrystals of siliceous substances, because using their

Tab. 3. Chemical compositions of carbon and silica derived from silicon-carbon

Tab. 3. Skład chemiczny węgla i krzemu uzyskanych z krzemo-węgla

SiO_2	Ca	Fe	Mg	Na	K	Al	P	B	H_2O
Carbon, %									
4.5	0.11	0.14	0.06	0.002	0.016	<0.1	0.02	0.0001	-
Silica, %									
88.4	0.002	0.013	0.012	0.12	0.003	<0.1	0.02	0.0001	11

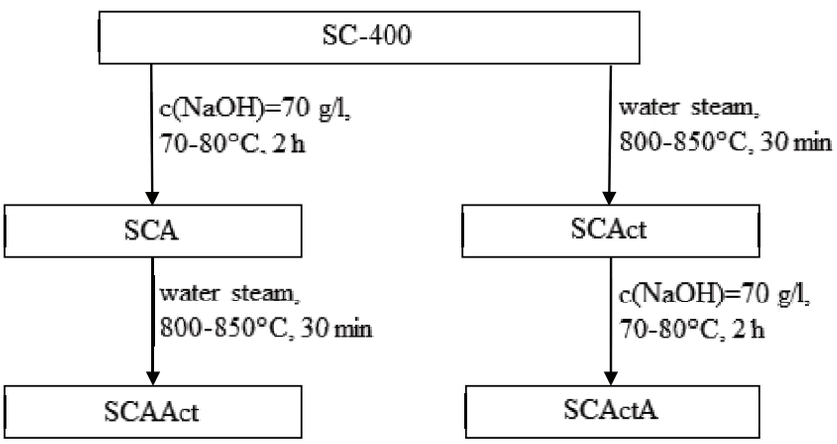

Fig. 4. Ways and conditions of silicon-carbon activation and the resulting products

Rys. 4. Sposoby i warunki aktywacji krzemo-węgla oraz uzyskane produkty

diffraction pattern interplanar space of 0.429 nm was calculated (Fig. 2e).

Using XRD it was possible to demonstrate that silicon-carbon SC-400 has an amorphous structure. The XRD pattern (Fig. 3) revealed the wide halo corresponding to the amorphous multicomponent carbon-containing materials. So, polynaphthene phase (82%) and another hydrocarbon phase (18%) were found from the main reflection with d ~ 0.47 nm and d ~ 0.8 nm, respectively, using iterative method with approximations based on experimental profiles of reflections for a number of standard substances [Efremova et al., 2008].

Using silicon-carbon in metallurgical processes

Due to the fact that silicon-carbon contains carbon and silica, it acts as a reducing agent and, at the same time, it is a raw material for production of silicon containing materials such are elemental silicon, silicon carbide, silicon alloys, for example, ferrosilicium.

It is well known that in order to produce elemental silicon it is required to mix carbon with silica at the stoichiometric ratio of $C:SiO_2$ = 1:2.5. To reach this ratio of main components silicon-carbon SC-400 was heated in oxidizing atmosphere (air) at 600°C during different time intervals. Silicon-carbon samples with different compositions listed in the Table 2 were prepared. These samples were subjected to 1% HCl treatment in order to reduce inorganic impurities content to 0.1% to obtain further silicon containing products with higher purity.

For comparison, amorphous silica and carbon were derived from silicon-carbon SC-400 by leaching with NaOH solutin (70 g/l). Carbon residue was filtrated and silica was precipitated from silicate solution by adding HCl. Both prepared products were washed with water and dried to remove moisture content. Their compositions are shown in the Table 3.

In both cases batch ingredients were mixed at the stoichiometric ratio of $C:SiO_2$=1:2.5. Next, briquettes were prepared using silicate glue and calcined at 300°C for 2 h. Elemental silicon was produced in a single-electrode furnace using the following experimental conditions: arc voltage, 80 V; current, 300–400 A; current density, 13 A/cm².

As a result elemental silicon with high purity (~ 98.8%) was produced.

Prepared silicon-carbon briquettes were used in the same metallurgical process of ferrosilicium production. Ferrosilicium corresponding to the grade FS75 was ob-

Tab. 4. Porous and sorption properties of silicon-carbon based materials

Tab. 4. Właściwości sorpcyjne i porowatość materiałów na bazie krzemo-węgla

Sample*	Specific surface area [m^2/g]	Average pore size [nm]	Pore volume[cm^3/g]	Adsorption of iodine [%]
SC-400	69	2.32	0.08	8.9
SCA	281	1.91	0.27	35.3
SCAct	303	1.22	0.18	27.9
SCActA	665	1.60	0.53	71.8

*SC-400 - silicon-carbon prepared by rice husk pyrolysis at 400ºC;
SCA – silicon-carbon treated with NaOH solution (70 g/l);
SCAct - silicon-carbon heated at 850°C under water vapour;
SCActA - silicon-carbon subjected to activation with water vapour followed by treatment with NaOH solution (70 g/l)

tained. However, this product has a significant advantage due to a low content of aluminum and titanium (less than 0.1%, each). This benefit allows using aluminum-free and titanium-free ferrosilicium to produce special kinds of steel.

Silicon-carbon from the rise husk was used for synthesis of silicon carbide of β-modification.

It is known that the ratio of filamentary crystals and dispersed powder of silicon carbide of β-modification (βSiC) and their structure and morphology depend essentially on the conditions of raw materials pretreatment before synthesis. Water and acid treatment of rice husk before pyrolysis was tested. The temperature of rice husk pyrolysis was changed from 400°C to 700°C. Silicon-carbon was charged into a graphite crucible (200 mm high and 80 mm in diameter). From the top to the bottom of the crucible an alundum tube was inserted throughout the whole silicon-carbon lay to supply argon. The βSiC synthesis was carried out in a high-frequency furnace at 1650±25°C for 30 minutes.

It was revealed that the water treatment of rice husk before pyrolysis resulted in formation of the mixture of filamentary crystals and dispersed powder silicon carbide of β-modification in the 1:1 ratio. Filamentary crystals were 0.1–1 micron in diameter and 20–200 micron long. The acid treatment of rice husk with 1–5% HCl solution at the same synthesis conditions resulted in loss of filamentary crystals yield and decrease in filamentary crystals and dispersed powder diameter to 0.01 micron. It was determined that low (400°C) and high (700°C) pyrolysis temperature leads to an increase in the dispersed powder content and a decrease in the filamentary crystals size and diameter. From this we conclude that the optimal pyrolysis temperature of the rise husk for silicon carbide production was 600°C.

Silicon-carbon-based porous materials as sorbents

The different porous carbon materials were prepared from silicon-carbon (Fig. 4) to study dynamics of their structure and porous characteristics depending on the way and conditions of silicon-carbon activation.

It was determined that silicon-carbon subjected to activation with water vapour followed by treatment with NaOH solution (70 g/l) has the largest specific surface area, the highest total pore volume and high adsorbtion of iodane (Table 4). Therefore, adsorption of heavy and rare metals from water solutions by this sorbent was examined in batch experiments.

Aqueous solutions of Cd(II), Pb(II), Cr(III), and Re(VII) were prepared using metal Cd, Pb, $Cr(NO_3)_3 \times 9H_2O$, and NH_4ReO_4, respectively. For equilibrium studies concentrations of metal ions were varied from 20 mg/l to 100 mg/l. Prepared solutions had the pH value of ca. 6, which was measured using EV-74 ionomer (Plant instrumentation, Byelorussia). For adsorption studies 0.2 g of investigated adsorbent were mixed with 20 ml of each of the prepared solutions in Erlenmeyer flasks and shaken in the rotary shaker at 150 rpm at the room temperature for 30 minutes (in case of Cd (II) for 90 minutes). Next, the mixtures were filtered and the concentrations of metal ions in the filtrate were analyzed using atomic absorption spectrometry (Agilent AA240FS, Agilent Technologies, USA).

Experimental results showed that the adsorption capacity and removal efficiency of metal ions were different in each cases. It was observed that ability of SCActA to remove metal ions decreases in the following order Cr(III) > Re(VII) > Pb(II) > Cd(II).

The sorption isotherms of metal ions were studied by fitting the obtained data to Freuindlich and Langmuir [Chen et al., 2011]. The Freuindlich and Lang-

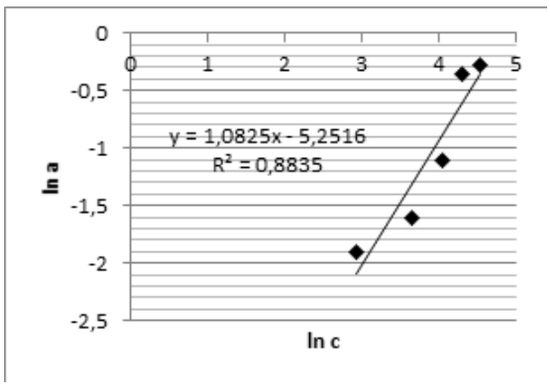

Fig. 5. Freunlich isotherm plot for Cd(II)

Rys. 5. Wykres izotermy Freunlicha dla Cd(II)

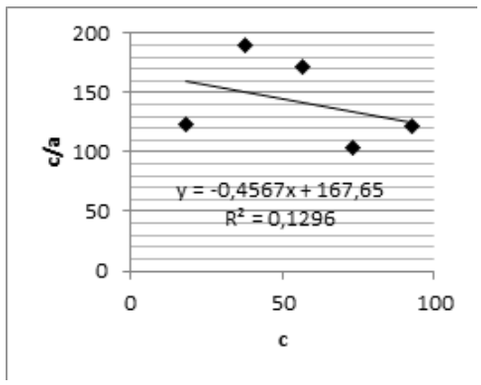

Fig. 6. Langmuir isotherm plot for Cd(II)

Rys. 6. Wykres izotermy Langmuira dla Cd(II)

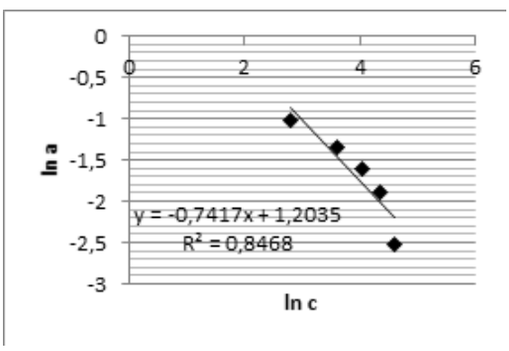

Fig. 7. Freunlich isotherm plot for Pb(II)

Rys. 7. Wykres izotermy Freunlicha dla Pb(II)

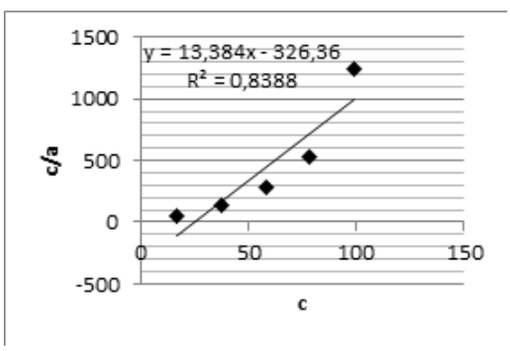

Fig. 8. Langmuir isotherm plot for Pb(II)

Rys. 8. Wykres izotermy Langmuira dla Pb(II)

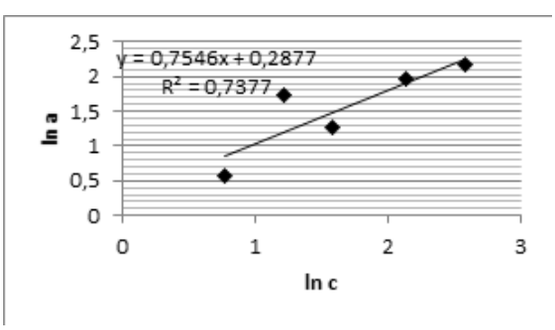

Fig. 9. Freunlich isotherm plot for Cr(III)

Rys. 9. Wykres izotermy Freunlicha dla Cr(III)

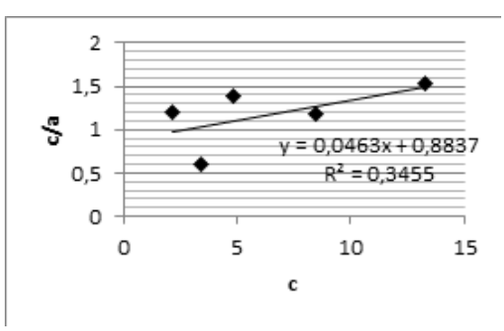

Fig. 10. Langmuir isotherm plot for Cr(III)

Rys. 10. Wykres izotermy Langmuira dla Cr(III)

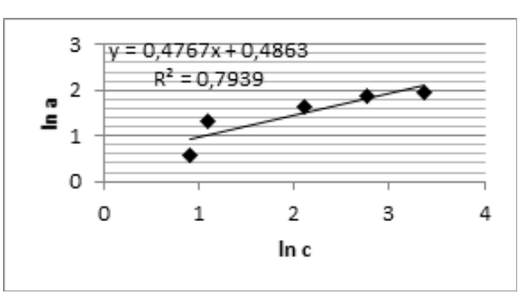

Fig. 11. Freunlich isotherm plot for Re(VII)

Rys. 11. Wykres izotermy Freunlicha dla Re(VII)

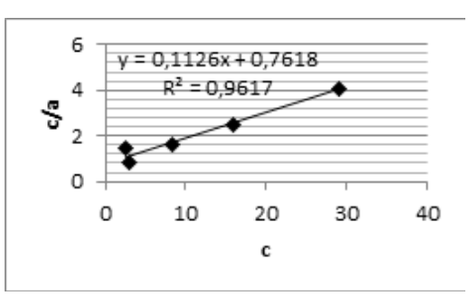

Fig. 12. Langmuir isotherm plot for Re(VII)

Rys. 12. Wykres izotermy Langmuira dla Re(VII)

Tab. 5. Freundlich isotherm parameters with SCActA

Tab. 5. Parametry izotermy Freundlicha dla SCActA

Metals	Freundlich isotherm parameters	SCActA
Cd(II)	Regression coefficient R^2	0.8835
	K_F	0.0052
	1/n	1.0825
Pb(II)	Regression coefficient R^2	0.8468
	K_F	3.3318
	1/n	-0.7417
Cr(III)	Regression coefficient R^2	0.7377
	K_F	1.3334
	1/n	0.7546
Re(VII)	Regression coefficient R^2	0.7939
	K_F	1.6263
	1/n	0.4767

muir isotherms are illustrated in Fig. 5-12 and their parameters are reported in Tables 5-6. It can be seen that Freuindlich isotherms fitted well the adsorption data for Cd(II) and Pb(II) while Langmuir isotherms fitted well the adsorption data for Pb(II) and Re(VII). Analysis of K_F and 1/n values shows that C (III) and Re(VII) adsorption with SCActA is favorable. However, higher regression coefficient values for heavy (Cd(II) and Pb(II)) metal ions are obtained from Freundlich model. According to this model the metal uptake by the tested sorbent decreases in the following order Pb(II)> Re(VII) > Cr(III) > Cd(II). Interaction energy between SCActA and Re(VII) ions is higher in comparison to other metal ions as KL value from Langmuir equilibrium shows. Table 7 compares experimental metal ions adsorption values of SCActA with calculated values using Langmuir and Freundlich models. It was found that both models show good agreement between the calculated values and experimental data of adsorption.

Using silicon-carbon as a feed additive

As it was mentioned above silicon-carbon is a homogenous mixture of amorphous and highly-active carbon and silica. It also contains trace amounts of several inorganic elements (iron, manganese, calcium, magnesium, potassium, and others) required in the diet of birds. Besides, it has good sorption properties. These factors allow considering it as a sorption-active feed additive, which can reduce the impact of toxic substances on the bird body, increase productivity, ensure environmental cleanliness and high quality of the manufactured products [Lipunova,2004]. The presence of silica contributes to granules strength and prevents them from caking.

Veterinary and toxicological assessment of silicon-carbon in laboratory animals and using bio-indication method showed that it is non-toxic and can be used as feed additives, which has been confirmed by the sanitary epidemiological control. It is recommended to use it in the diet for the laying hens and chicken broilers in concentration from 1 to 6%. In studies with chicks and hens it was determined that silicon-carbon neutralizes the toxicity of natural feed and promotes weight gain. It was found that feeding chicks and hens on the mixed fodder with addition of 3% of the new feed additive increased the egg-laying capacity of the laying hens (by 8.6%) and decreased the egg-breakage (by 31%), the hens mortality (by 28%) and sanitary slaughtering (by 13%).

Organic product of rice husk pyrolysis as a floatation reagent

Upon setting-out the liquid product from the pyrolysis of rice husk segregated into two layers. The top layer was light brown liquid, while the lower one was tar oil. In this study the top layer was investigated. Fig. 13 shows the chromatogram of the liquid product of the rice husk pyrolysis. Analysis of the resulting mass

Tab. 6. Langmuir isotherm parameters with SCActA

Tab. 6. Parametry izotermy Langmuira dla SCActA

Metals	Langmuir isotherm parameters	SCAAct
Cd(II)	Regression coefficient R^2	0.1296
	a_m	-2.1896
	K_L	-0.0027
Pb(II)	Regression coefficient R^2	0.8388
	a_m	0.0747
	K_L	-0.0410
Cr(III)	Regression coefficient R^2	0.3455
	a_m	21.5983
	K_L	0.0524
Re(VII)	Regression coefficient R^2	0.9617
	a_m	8.88
	K_L	0.1478

Tab. 7. Comparison of experimental metal ions adsorption values of SCActA with calculated values using Langmuir and Freundlich models

Tab. 7. Porównanie wartości adsorpcji doświadczalnej jonów metali dla SCActA z wartościami obliczeniowymi z wykorzystaniem modeli Langmuira i Freundlicha

Metals	C_o [mg/l]	C [mg/l]	$a_{experimental}$ [mg/g]	$a_{calculated}$ [mg/g]	
				Langmuir	Freundlich
Cd(II)	20	18.5	0.15	0.12	0.12
	40	38	0.2	0.25	0.27
	60	56.7	0.33	0.40	0.41
	80	73	0.7	0.54	0.54
	100	92.4	0.76	0.74	0.70
Pb(II)	20	16.4	0.36	-0.15	0.42
	40	37.4	0.26	0.21	0.23
	60	58	0.2	0.13	0.16
	80	78.5	0.15	0.11	0.13
	100	99.2	0.08	0.10	0.11
Cr(III)	20	2.16	1.784	2.20	2.38
	40	4.85	3.515	4.38	4.39
	60	3.38	5.662	3.25	3.34
	80	8.5	7.15	6.65	6.70
	100	13.29	8.671	8.87	9.39
Re(VII)	20	2.5	1.75	2.40	2.52
	40	3	3.7	2.73	2.75
	60	8.3	5.17	4.89	4.46
	80	16	6.4	6.24	6.10
	100	29	7.1	7.20	8.10

spectra was performed basing on a computer search against a data base containing known mass spectrometric patterns of different compounds. Table 8 lists the identified substances and amount thereof.

Organic product was tested as a floatation reagent for enrichment of raw materials.

For this study we have chosen rebellious lead-zinc ore of Shalkiya deposit, which contains 1.57% lead and 4.28% zinc. According to X-ray analysis, these metals

Tab. 8. The composition of the liquid product of rice husk pyrolysis

Tab. 8. Skład produktu płynnego po pirolizie łusek ryżowych

Substances	Area [%]
1	2
Phenol, 2,6-dimethoxy-	0.14
Phenol, 4-ethyl-2-methoxy-	0.11
Phenol, 2-methoxy-4-methyl-	0.26
Phenol, 2-ethyl-	0.13
Phenol,2,5-dimethyl-	0.08
Phenol,2-methoxy-	0.73
Phenol,4-methyl-	0.25
Phenol,2-methyl-	0.16
Phenol,	0.65
2-Cyclopenten-l-one, 3-ethyl-2-hydroxy-	0.07
2-Cyclopenten-l-one, 2,3-dimethyl-	0.05
2-Cyclopenten-l-one, 2-hydroxy-3-methyl-	0.3
2-Cyclopenten-l-one, 3-methyl-	0.08
2-Butanone, 3,3-dimethyl-	0.02
Butyrolactone	0.19
Ethanone, 1-(2-furanyl)-	0.06
2-Cyclopenten-l-one, 2-methyl	0.1
1	2
2-Propanone, 1-(acetyloxy)-	0.24
2-Cyclopenten-l-one	0.11
1-Hydroxy-2-butanone	0.49
2-Propanone, 1-hydroxy-	1.39
Acetic acid	5.72
Propanoic acid	0.69
Hexanoic acid	0.06
Pentanoic acid	0.08
Formic acid	0.05
1,2 dicarboxylic acid	0.02
1-Propanol	0.05
Acetaldehyde, methoxy-	0.07
Homovanillylalcohol	0.07
Furfural	0.13
3-Aminopiperidin-2-one	0.16
2-Furanmetanol	0.4
Propanamide, 2-methyl	0.15
Others	0.9

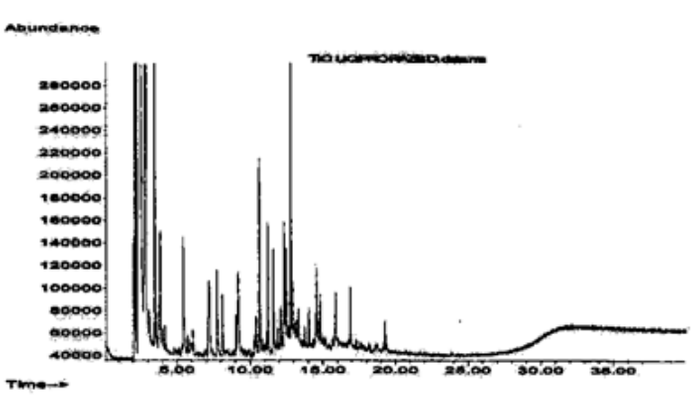

Fig. 13. Chromatogram of a liquid product of rice husk pyrolysis

Rys. 13. Chromatogram produktu płynnego po pirolizie łusek ryżowych

Tab. 9. The results of the closed experiments per standard mode with common MIBK blowing agent

Tab. 9. Wyniki zamkniętych eksperymentów w trybie standardowym z wykorzystaniem powszechnego środka porotwórczego MIBK

Product name	Yield [%]	Content [%]		Extraction [%]	
		Pb	Zn	Pb	Zn
Lead concentrate	2.07	45.27	6.25	60.73	3.13
Zinc concentrate	4.94	0.70	53.34	1.23	62.14
Final tailing	92.99	0.64	1.58	38.04	34.73
Head ore	100.0	1.57	4.23	100.0	100.0

Tab. 10. The results of the closed experiments with the organic product as a blowing agent

Tab. 10. Wyniki zamkniętych eksperymentów z wykorzystaniem produktu organicznego jako środka porotwórczego

Product name	Yield [%]	Content [%]		Extraction [%]	
		Pb	Zn	Pb	Zn
Lead concentrate	2.1	44.95	6.2	60.34	3.10
Zinc concentrate	4.9	0.70	53.5	2.19	62.37
Final tailing	93.0	0.63	1.56	37.47	34.53
Head ore	100.0	1.56	4.20	100.0	100.0

are mainly in the sulfide minerals state (93% lead and 97.08% zinc).

During the comparative open experiments using methyl isobutyl ketone (MIBK) as a standard blowing agent and the organic product following reagent regime was worked out which was used for the closed experimentation:

- liquid glass – 200 g/t of ore (agitation for 2 minutes);
- zinc sulfate – 400 g/t of ore (agitation for 2 minutes);
- sodium cyanide – 36 g/t of ore in the experiments using MIBK and 20 g/t of ore in the experiments using organic material instead of MIBK (1 minute agitation);
- 500 g/ton sodium sulfide in the experiments using MIBK and 400 g/t of ore in the experiments using organic material instead of MIBK;
- Ksantogenat – 86 g/t of ore in the rough flotation and 50 g/t of ore in the scavenger one;
- MIBK blowing agent – 90 g/t of ore in the rough flotation and 50 g/t of ore in the scavenger one;
- organic product – 5 liters/ton of ore.

The concentrates were taken in batches every 2 minutes.

Results of the closed experiments are presented in the Tables 9-10.

As a result of standard mode closed flotation experiment two concentrates were produced: 1) a lead concentrate that contains 45.27% of lead and 6.25% of zinc; upon extraction the content of lead was 60.73%; 2) zinc concentrate containing 53.34% of zinc and 0.70% of lead; upon extraction the content of zinc reached 62.14%.

The results of the experiment using the organic product as a blowing agent showed that the obtained parameters were comparable to the standard mode. In case of the standard mode experiment a total recovery of lead and zinc in the same concentrates was 122.87%, while using the organic product as a blowing agent a total recovery was 122.71%. Therefore, it was found that organic product has properties of a blowing agent similar to standard reagent such as methyl isobutyl ketone. However, the reaction conditions should be adjusted in each individual case, i.e. depending on the composition of the ore.

Conclusion

In this study silicon-carbon and liquid organic product was produced by rice husk pyrolysis at 400°C under off-gas atmosphere for 30 min. It was found that silicon-carbon is a suitable raw material for production of different silicon containing products. It is required to reach the stoichiometric ratio of $C:SiO_2 = 1:2.5$ in silicon-carbon composition and remove inorganic impurity from it by treatment with 1% HCl to obtain elemental silicon with high purity (~98.8%) and aluminum-free and titanium-free ferrosilicium. For production of silicon carbide of β-modification the following steps are recommended: water treatment of rice husk, its pyrolysis at 600°C and βSiC synthesis using prepared silicon-carbon at 1650°C for 30 minutes. It was determined that silicon-carbon treated by water vapour followed by treatment with NaOH solution (70

g/l) has the best adsorbtion properties and it is a potential sorbent for the removal of rare and heavy metals ions from water media. It has higher interaction energy with Re (VII) ions comparing to tested Cr (III), Pb (II), and Cd (II) ions. Both Langmuir and Freundlich models fitted well the experimental data of adsorption for these metal ions. Moreover, silicon-carbon is non-toxic and it can be used as a feed additive for agricultural birds. It allows to increase the egg-laying capacity of the laying hens and decrease the egg-breakage, the hens mortality and sanitary slaughtering. Liquid organic product has properties of a blowing agent similar to standard reagent such as methyl isobutyl ketone and it can be used in floatation of lead-zinc ores. All in all, results of this study illustrate a possibility of setting a plant for rice husk recycling and simultaneous production of competitive products for different sectors of the economy.

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Abstrakt

Stały materiał węglowy i produkt płynny wytworzono prowadząc pirolizę łusek ryżu. Do zbadania składu otrzymanych materiałów wykorzystano odpowiednio analizę chemiczną i GC-MS. W celu zbadania struktury i budowy materiału węglowego zastosowano badania rentgenowskie, SEM, TEM i BET. Stwierdzono, że produkt stały jest kompozytem złożonym z węgla (52%) i nanocząstek dwutlenku krzemu (31%). Dlatego został nazwany krzemo-węglem. Produktem ciekłym był roztwór wodny zawierający różne związki organiczne (kwasy karboksylowe, fenole, ketony, alkohole i etery, cykliczne węglowodory alifatyczne, związki heterocykliczne). Zbadano możliwość nanoszenia stałego materiału węglowego jako środka redukującego i sorbentu, natomiast zastosowanie dla ciekłego produktu organicznego jako odczynnika flotacyjnego weryfikowano w procesie elektrotermicznego wytapiania oraz w procesach sorpcji i flotacji. Przeprowadzono również badania weterynaryjne i toksykologiczne w celu oceny toksyczności stałego materiału węglowego i możliwości jego zastosowania jako dodatku paszowego. Wykazano, że ze względu na skład chemiczny, krzemo-węgiel stanowi kompleksowy surowiec do produkcji metalurgicznego krzemu, węglika krzemu oraz żelazokrzemu bez dodatku glinu i tytanu. Produkowany sorbent miał dużą zdolność adsorpcji metali rzadkich i ciężkich. Stały materiał węglowy, który okazał się być nietoksyczny, był skutecznym dodatkiem do pasz poprawiając jakość kur niosek i brojlerów. Produkt ciekły wykazywał właściwości środka porotwórczego we flotacji rud ołowiu i cynku. Stwierdzono, że zarówno stały jak i ciekły materiał węglowy pochodzący z łupin ryżowych są ekonomicznie efektywnymi materiałami dla różnych procesów technologicznych i rolnictwa.

Słowa kluczowe: łuski ryżowe, piroliza, krzemo-węgiel, produkty organiczne, metalurgia, rolnictwo