Activated Carbons from the Compressed Plant Materials (Coconut Shell) and Copolymers of Furfural

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Abstract

This paper dwells upon the physical and chemical properties of activated carbons based on compressed plant materials (coconut shell) and on furfural copolymers, the paper also gives the results of their elemental analysis by ICP-MS method, the structure and morphology of the obtained sorbents have been determined by scanning electron microscopy. The specific surface of the obtained activated carbons has shown that a sorbent based on coconut shell has the highest specific surface (Sspecific surface = 1100 m²/g) if compared to the sorbent based on copolymers of furfural (Sspecific surface = 653 m²/g). However, the sorbent based on furfural copolymers has a higher mechanical resistance to abrasion (98%) and a low ash content (0.3%) compared to the indices of the sorbent based on coconut shell (mechanical strength = 92%, ash content = 2.5%). The study of the structure and morphology of the obtained activated carbons has shown that within the structure of the sorbent based on the copolymers of furfural mesopores predominate together with micropores, when in the structure of the sorbents based on coconut shells micropores are mostly predominant. The elemental analysis of the adsorbents has shown that they are mainly composed of carbon, but there were also some trace amounts of some other elements.

Keywords: activated carbon, sorbent, furfural copolymers, coconut shell, mesopores micropores, specific surface, sorption activity by cyanide complex of the gold

Introduction

Currently plant waste is processed differently to obtain valuable products, particularly it is usually processed in a mechanochemical way while obtaining basic constructions; in a chemical way while getting artificial fabrics, smokeless powder, motion picture films and photographic films, celluloid and other natural and man-made polymers, as well as alcohols, acids, solvents, resin, fodder yeast, furfural, ethanol, amino acids, vitamins and other substances. At the same time plant waste is a promising and annually renewable raw material useful for deriving new sorbents which have different properties of the porous structure, which determines the possibilities of their wide sphere of application. Using plant waste we can obtain sorbents with the properties similar to those obtained from coal, peat and refinery waste (Mukhin, Lupascu et al., 2014).

Activated carbons are wide-spread and widely used adsorbents in many fields. They are carbonic solid units (bodies) with a developed porous structure and high specific surface, due to this they obtain their special sorption properties as capacity to absorb the substances of various nature from liquids and gases. The more porous the structure of activated carbon is, the greater its sorption properties are (Yun et al., 1998).

Along with that, activated carbons enable us to meet the wide spectrum of technological challenges in mining, processing industries as well as in power engineering and agriculture. The adsorptive technologies application sphere involving using activated carbons is becoming wider, which is largely due to three reasons: firstly, activated carbons provide the opportunity to get production of the goods of high purity for the whole number of manufactures; secondly, adsorbents may help to introduce many advanced technologies into the production process, the technologies with the increased intensity and, thirdly, they allow us to efficiently resolve the most severe problems of biosphere protection from polluting emissions (Mukhin and Klushin, 2012).

There are two types of activation processes for the production of activated carbons from carbon-containing materials: gas-vapor activation and chemical activation. Gas-vapor activation includes a two-stage process, i.e. carbonization in the inert atmosphere, and then activation with a use of water vapor, oxygen or carbon dioxide as an activating agent (Yuen and Hameed, 2009). In the process of chemical activation reagents such as potassium hydroxide, phosphoric acid and zinc chloride are used as an activating agent, herein the

Tab. 1. The yield of furfural obtained from pentosane raw materials

Tab. 1. Uzysk furoaldehydu uzyskanego z pentozanu

Raw material	Content, mass %		Average furfural yield, mass %	
	from pentosans	from uronic acids	theoretical	practical
Corncob cores	30–35	7.42	24	11
Husk:				
Oats	32–35	-	25	11
Cotton plant -seed	21–27	7.73	18	9
Shuck:				
Sunflower-seed	18–25	11.3	16	9
Rice	17–20	4.39	15	8
Bagasse	23–25	-	18	9
Wood:				
birch	22–25	5.71	17	8
aspen	16–20	7.96	13	7
Oak (tan-bark waste)	19–20	5.08	14	6

carbonization and activation both take place (Ncibi et al., 2009).

In our research we have applied gas-vapor activation, wherein the carbonization was carried out in the inert atmosphere of argon at 800°C and activation – in water steam at 850°C. As a raw material for activated carbons preparation we used coconut shells and furfural derived from the local plant agricultural waste of the Republic of Kazakhstan. It should be noted that the activated carbons based on coconut shell are widely available on the world market and they are one type of the standards of high-quality carbon sorbent. The conducted research works were also aimed at import substitution with the focus on local raw materials in such an important sphere like the preparation and use of activated carbons which are important in the economics and the ecology of each country, this fact determines the novelty of this work.

Furfural is obtained by boiling various plant and agricultural wastes (sunflower stems, corncobs, straw, shorts and others) with sulfuric acid. Besides, hydrolysis of hemicellulose, polysaccharides of plant cell walls takes place, and the resulting pentosan-containing feedstock is subjected to dehydration under the action of sulfuric acid, which leads to the formation of furfural (Dzhilkrist, 1996). In the production of furfural pentosanes hydrolysis process and pentose dehydration are carried out simultaneously without isolation of the pentose hydrolyzate, which is related to the possibility of obtaining of a higher yield of the desired product in this combined process (Gravitis et al., 2001). Theoretically possible yield of furfural from pentosans makes up 73%, and from pentose – 64%. In practice, furfural yield is substantially lower due to its conversion into other compounds (Table 1).

The purpose of this work is to obtain AC based on copolymers of furfural, the study of physical and chemical characteristics of the obtained sorbent, the study of the structure and morphology of the material obtained by scanning electron microscopy, determination of its elemental composition by ICP-MS. All these results we compared with the results of activated carbon, based on coconut shell.

Experimental part

Methods of obtaining activated sorbents based on furfural

Activated carbons of spherical forms were prepared by mixing polyester resin with furfural in the acidic medium and dispersing the mixture onto the layer of viscous liquid at room temperature, ensuring mixture gelatinization. The resulting product was subjected to carbonization in the inert atmosphere of argon at 800°C, and then to the activation process in water steam at 850°C (Kishibayev et al., 2013).

As an illustrative example for this, figure 1 shows the external view of a raw material for preparation of activated carbon based on a copolymer of furfural, and finished product – AC.

The method of activated carbons preparation with the activated carbons based on vegetable raw materials (coconut shells)

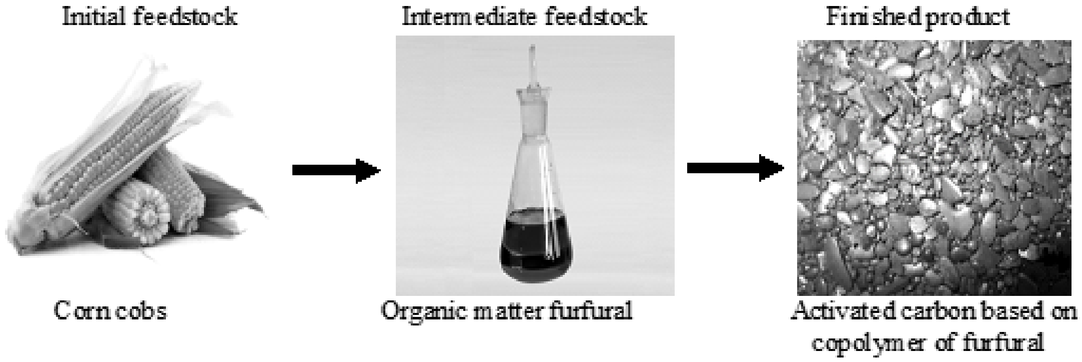

Fig. 1. External view of raw material and activated carbon based on copolymers of furfural

Rys. 1. Widok zewnętrzny surowca oraz węgla aktywnego opartego na kopolimerach z furoaldehydu

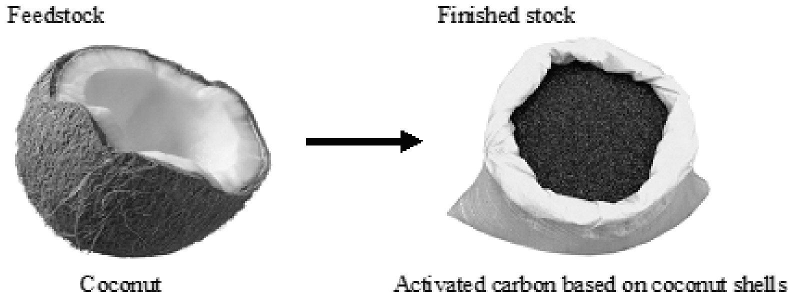

Fig. 2. The raw material and activated carbons based on coconut shells

Rys. 2. Surowiec i węgle aktywne oparte na łupinach kokosowych

The sorbents based on coconut shells were prepared as follows.

1. The coconut shells were crushed with the sowing waste particle of 1–2 mm.
2. The obtained fractions of coconut shells were subjected to heat treatment in the inert atmosphere of argon at the temperature of 700°C.
3. The activation with scalding steam was conducted at the temperature of 800°C.
4. The obtained ACs were analyzed.

In figure 2 one can see the raw material for preparation of activated carbon based on coconut shells, also the finished product – activated carbon on such a basis.

The study of specific surface of sorbents by the method of Brunauer–Emmett–Taylor (BET)

By changing the thermal conductivity of the gas stream passing through the tube of the measured sample we have determined the amount of nitrogen adsorbed by the surface of the sorbent gas mixture while cooling it with the liquid nitrogen and subsequently desorbing during the heating of the sample at the room temperature. By varying the concentration of the adsorbed gas (nitrogen) of the mixture we obtained several adsorption indices corresponding to the different concentrations of nitrogen. Further we have created the adsorption isotherm and calculated the surface area of the sample using the peak area indices (Dreving and Muttik, 1990).

Mechanical abrasion resistance test in the roll

Figure 3 shows the equipment for determining the mechanical strength during carbon sorbent particles attrition and their attrition losses. The device consists of a roll (stainless steel) fitted from the inside with the side outlet or pipe bend and the lid. The roll can be set in three different positions: on the top – for loading, to the bottom – for unloading and horizontal – for operation.

The roll is rotated by the motor with gearbox, which is controlled by the timer.

1) We take a tested sample of carbon sorbent at the amount of about 100 g;
2) We sifted the sample out through N°20 screen with the size of 0.5 mm;
3) Dried it in the oven at 100°C for 3 hours;
4) Cooled it in the desiccator;
5) We weighed 100 grams (the accuracy of

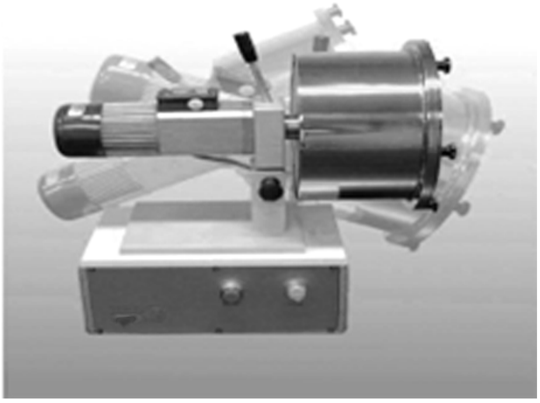

Fig. 3. Setting the test on mechanical resistance to abrasion in a roll

Rys. 3. Ustawienia do testu na odporność mechaniczną na abrazję w walcu

Tab. 2. Physico-chemical characteristics of AC on the basis of coconut shells and furfural copolymers

Tab. 2. Charakterystyka fizykochemiczna węgla aktywnego na podstawie łupin kokosowych oraz kopolimerów z furoaldehydu

Index	Sorbent based on copolymers of furfural	Sorbent based on coconut shells
Feedstock	Furfural	Coconut shells
Specific surface, m^2/gr	653	1100
Ash content, %	0.3	2.5
Abrasion resistance according to the International standard ("GOST" 16188-70), %	98	92
Micropore volume, cm^3/gr	0.26	0.36
Mesopore volume, cm^3/gr	0.50	0.20

0.01 g) of the carbon sorbent and placed the sorbent into the roll. The lid is closed then.

6) Then the roll rotated for 30 minutes at 60 ± 5 RPM.

7) After the test, the sample was again sifted through the N° 20 screen with the size of 0.5 mm, the remaining material was weighed.

Abrasion losses were defined as follows (Formula 1):

$$Y\% = \left(\frac{P_1 - P_2}{P_1} \right) \times 100 \qquad (1)$$

P1 – the initial mass of carbon sorbent;
P2 – the mass remaining in the screen.

Scanning electron microscopy (SEM). Sorbents study was also performed on scanning electron microscope Quanta 3D 200i Dual system (FEI Company) in the National Nanotechnology Open Type Laboratory of Al-Farabi National University. The advantage of scanning electron microscopy is the ability to obtain a visual "three-dimensional" image of a very wide range of increase indices.

Elemental analysis of the sorbent content was conducted through the mass spectrometry method (ICP-MS) with inductively coupled plasma ICP Mass Spectrometer Varian 820-MS.

For dissolution the necessary solution is chosen, the choice is easier if one has the antecedent data within the sample content. As it is known, chemically resistant inorganic substances may be dissolved in hydrochloric acid or hydrofluoric acid, as well as the mixtures thereof. The dishes for liquid samples of modern ICP-MS are made of the structural materials resistant to corrosion. Organic substances may be subjected to thermal decomposition (digestion), followed by acid dissolution (Nelms, 2005; Pupyshev and Surikov, 2006).

Results and discussion

The results of physico-chemical characteristics of activated carbons are given in Table 2.

From the obtained results it is obvious that the activated sorbent on the basis of coconut shells ($S_{specific\ surface}$ = 1100 m^2/gr) has a more specific surface in comparison with the ACs on the basis of furfural copolymers ($S_{specific\ surface}$ = 653 m^2/gr). It is

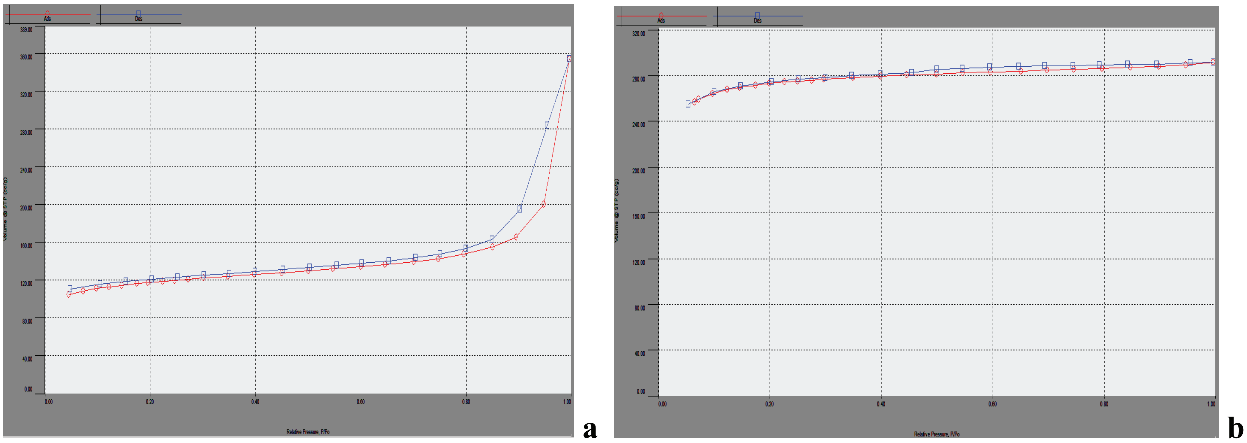

Fig. 4. Adsorption isotherms for activated carbons: a) based on copolymers of furfural; b) based on coconut shells

Rys. 4. Izotermy adsorpcji dla węgla aktywnego: a) oparte na kopolimerach z furoaldehydu; b) oparte na łupinach kokosowych

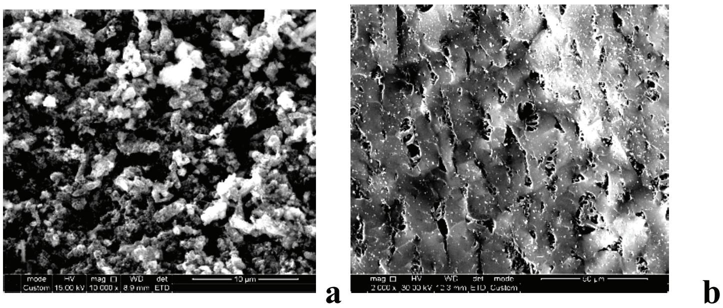

Fig. 5. Micrographs of AC: a) sorbent based on furfural copolymers, b) sorbent based on coconut shells

Rys. 5. Mikrografy węgla aktywnego: a) sorbent oparty na kopolimerach z furoaldehydu; b) sorbent oparty na łupinach kokosowych

explained by the different ratio of micro- and mesopores of the derived sorbents. It is necessary to note that the sorbent based on copolymers of furfural has less ash percentage and has the highest mechanical resistance compared to the sorbent on the basis of coconut shells. Mechanical resistance of these ACs is of a high importance for their reactivation and returning to technological procedure.

The activated carbons obtained by using the new modes and on the basis of domestic raw materials of Kazakhstan, taking into consideration their main technological characteristics, are at the same or at a higher level than similar sorbents produced by leading foreign companies and firms. Thus, the ACs FAS-G (TC 6-16-28-1578-94 Active coal FAS-G ENPO "Inorganic" production (Russia)) based on copolymers of furfural have the micropore volume of 0.40 cm^3/g; with the strength of 92%; and ash content of 2%) and coconut shell-based AC GCN 830 manufactured by Norit (Netherlands) has the micropore volume of 0.35 cm^3/g; 95% – strength; and ash content of 3% (Mukhin, 2003).

Figure 4 shows AC adsorption isotherms with the AC based on furfural copolymers and coconut shells.

From the obtained adsorption isotherms it is seen that the activated carbon based on copolymers of furfural (Figure 4 a) is characterized by a porous structure with a preferential development of mesopores (2–50 nm). AC adsorption isotherm with the AC based on coconut shells (Figure 4 b) is characterized by a predominant development of micropores (0.8–1.0 nm).

Figure 5 shows the results of electron-microscopic research of the obtained AC.

Micrograph of the sorbent based on furfural copolymers (Figure 5a) indicates that the surface has a cellular structure with a large number of pores and channels on the surface, the size of which ranges from 20 nm to 2 microns. From the micrograph of the sorbent based on coconut shells (Figure 5b) it is seen that the surface has a fractured structure with a large number of slight pores. The pore size ranges from 2 to 10 nm.

Tab. 3. The elemental composition of the AC based on copolymers of furfural and coconut shells

Tab. 3. Skład pierwiastkowy węgla aktywnego opartego na kopolimerach z furoaldehydu oraz na łupinach kokosowych

Element content	Sorbent based on the copolymers of furfural	Sorbent based on coconut shells
C (wt.%)	84.490	95.350
S (wt.%)	0.680	0.327
Li (mg/kg)	0.129	0.131
B (mg/kg)	1.406	10.396
Na (mg/kg)	49.333	531.188
Mg (mg/kg)	18.483	271.022
Al (mg/kg)	68.229	77.787
Si (mg/kg)	0	742.574
P (mg/kg)	998.542	792.079
K (mg/kg)	61.738	8632.079
Ca (mg/kg)	68.040	190.693
Sc (mg/kg)	0	0.001
Ti (mg/kg)	0.877	1.238
V (mg/kg)	0.106	0
Cr (mg/kg)	9.685	0.253
Mn (mg/kg)	1.362	4.145
Fe (mg/kg)	70.044	124.490
Co (mg/kg)	0.374	0
Ni (mg/kg)	2.772	0.078
Cu (mg/kg)	111.920	7.785
Zn (mg/kg)	903.930	0.719
Ga (mg/kg)	0.025	0.032
As (mg/kg)	2.011	0.447
Se (mg/kg)	0.030	3.095
Ba (mg/kg)	0.666	10.040

In table 3 the results of the elemental composition of the obtained sorbents are shown.

From these data it is evident that the sorbent based on coconut shell has the highest content of carbon (C (carbon) = 95.350 wt.%) compared with the sorbent based on furfural copolymers (C (carbon) = 84.490 wt.%). Besides, both sorbents include various amounts of other elements, and their content in the sorbent based on coconut shell is substantially higher which is, of course, due to the nature of the feedstock. It should be noted that in the sorbent based on coconut shell, V and Co are absent, Si and Sc are present (compared with the sorbent based on furfural copolymers). This can be explained by the fact that these metals are included in the structure of the carbon matrix and secured there in various types of links, including coordination.

Taking into account that the Republic of Kazakhstan is one of the leading gold-producing countries of the world, and in this regard it has a high need of domestic high-strength sorbents derived from local raw materials for coal-sorption technologies for extracting gold from ore, the obtained sorbents have been tested in the extraction process of gold from cyanide solution. Figure 6 shows the kinetics of extraction of gold from cyanide solution using the obtained sorbents.

From figure 6 is obvious that the degree of extraction of gold from cyanide solutions used in production, with the AC from copolymers of furfural practically matches that index with the AC from coconut shell. This can be explained by the developed micropore volume with the dimensions of 0.8-1.0 nm, which is favorable for sorption of cyanide complexes of gold, and with a large volume of mesopores (0.20-0.26 cm^3/g), that are responsible for the kinetics of both carbonaceous sorbents. The gold recovery level after 48 hours with the help of the activated carbon based on copolymers of furfural reached 98.7%, and with the help of the activated carbon based on coconut shell for the same period it made up 98.9 %, which indicates their high adsorption capacity for gold cyanide complex.

Conclusion

Thus, we have obtained activated carbons based on furfural copolymers and coconut shell, a comprehensive comparative analysis of physi-

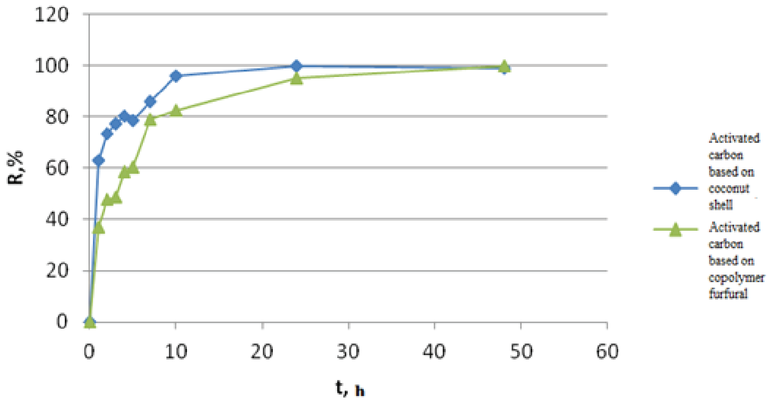

Fig. 6. The kinetic curve of gold extraction from cyanide solutions with sorption using the obtained activated carbons

Rys. 6. Krzywa kinetyki odzysku złota z roztworu cyjanku z sorpcją przy zastosowaniu otrzymanych węgli aktywnych

co-chemical properties of the porous structure and the adsorption capacity for gold cyanide complex has been conducted.

It has been shown that the sorbent based on coconut shell had the highest specific surface (Sspecific surface = 1100 m^2/g) compared to the sorbent based on copolymers of furfural (Sspecific surface = 653 m^2/g).

The sorbent based on copolymers of furfural had low percentage of ash content and possessed a high mechanical strength to abrasion as compared with the sorbent based on coconut shell.

The morphology and structure of the obtained sorbents have been studied by scanning electron microscopy that allowed to reveal the nature of the surface structure of the sorbent grains.

We have also determined the elemental composition of the obtained sorbents by mass spectrometry with inductively coupled plasma and revealed the differences in the content of some elements in them.

It was determined that both obtained sorbents had a high adsorption capacity for gold cyanide complex.

The study results suggest that the obtained adsorbents can be used in coal-sorption technology for extracting precious metals, particularly for gold, and for various liquid - phase processes, including waste-water treatment from various contaminants. The performed study suggests the possibility of replacing the expensive imported activated carbon from coconut shells for domestic high-performance adsorbents based on copolymers of furfural, made from local raw materials of the Republic of Kazakhstan.

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Aktywny węgiel z materiałów roślinnych (łupiny kokosowe) oraz kopolimery z furoaldehydu

Artykuł dotyczy fizycznych i chemicznych właściwości aktywnego węgla z materiałów roślinnych (łupiny kokosowe) oraz kopolimerów z furoaldehydu. Ponadto przedstawiono w artykule wyniki ich składów pierwiastkowych uzyskanych za pomocą metody ICP-MS a także struktury i morfologii otrzymanych sorbentów za pomocą elektronowego mikroskopu skaningowego. Powierzchnia właściwa otrzymanego aktywnego węgla wykazała, że sorbent bazujący na skorupach kokosowych ma największą powierzchnię właściwą (Sspecific surface = 1100 m²/g) porównując ją z sorbentem opartym na kopolimerach z furoaldehydu (Sspecific surface = 653 m²/g). Jednakże, sorbent oparty o kopolimery z furoaldehydu mają większą odporność na abrazję (98%) i niską zawartość popiołu (0.3%) w porównaniu do wskaźników sorbentu opartego o łupiny kokosowe (wytrzymałość mechaniczna = 92%, zawartość popiołu = 2.5%). Badanie struktury i morfologii otrzymanego węgla aktywnego wykazało, że wewnątrz struktury sorbentu opartego na kopolimerach z furo aldehydu jest równie wiele mezoporów, jak i mikroporów, podczas gdy struktura sorbentów bazujących na łupinach kokosowych jest zdominowana głownie przez mikropory. Analiza pierwiastkowa adsorbentów wykazała, że są one głównie złożone z węgla, ale zawierają również nieco śladowych ilości innych pierwiastków.

Słowa klucze: węgiel aktywny, sorbent, kopolimery z furoaldehydu, łupiny kokosowe, mezopory, mikropory, powierzchnia właściwa, aktywacja sorpcyjna przez cyjankowe związki złota