Vegetable Waste as Perspective Raw Materials for the Production of Carbon Adsorbents

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Abstract

As it is known active carbons are universal sorbents allowing to solve a wide range of industrial tasks, problems of environmental protection and a human health. New perspective raw material for active carbons production (AC) is different plant wastes including waste wood, the volume of which is constantly increasing, and the only way of their dsposal is incineration.

In recent years we developed three main new technologies of AC on base of plant raw materials and showed the prospects of their use in environmental technologies. We made examples of developing new active carbons and their implementation in practice of the environmental technologies. In particular, it is shown to be effective in cleaning the exhaust air, water treatment, soil rehabilitation and other fields.

Keywords: active carbons, environmental engineering, vegetable raw material, wood waste

Introduction

The progressing pollution of environment has made the environmental safety an important constituent of the national safety as a whole.

Today practically all the planet and especially the regions of mass residence of people are threatened by serious environmental problems main of which are radiation pollution of territories, soil pollution by acid precipitation, soil poisoning by chemicals and pesticides, oil spills overland and asea and atmosphere destruction. Biosphere pollution sharply deteriorate people's quality of life; thus, according to data of World Health Organization (2002) the factors influencing the human health depend on: nutrition and way of life – 51%, ecology – 39%, medicine – 10%.

In the light of the above said a special consideration must be given to the environmental safety of agriculture providing people with food as the soils of farmland include only 6% of all the territory of land and the quantity of people in the end of the XXI century will be 10 billion.

The issues of global environmental contamination have been raised earlier by Russian scientist, professor of Mendeleev Chemical Technological Institute N. V. Keltsev, who offered a main track of solving the problem-. He wrote: "At present when the question of life and death is vital not only for the army but to all the humanity which is anxious by a catastrophic pollution of biosphere it is time to apply again for help for adsorption - one of the most effective methods of environment protection from contamination".

By reason of their physical-chemical properties the carbon adsorbents (active carbons) are unique and ideal sorption materials allowing to solve a wide range of questions for providing a chemical and biological safety of a human safety, environment and infrastructure [1].

Active carbons (AC) are high porous substances received in the form of grains or powder on base of different carbon containing raw materials possessing a developed inner surface (up to 2500 m2/g) and high adsorbing capacities of impurities in purified media (air, gases, water and other liquids, soil).

A special interest present various vegetable wastes as constantly renewable source of raw material.

We developed the technologies of AC production from main many ton vegetable wastes: straw, nutshell and stones of fruit trees, sawdust and hydrolyses products of corn stumps and husk of sunflower; showed the efficiency of their application in a number of environmental engineering.

Active Carbons on Base of Straw (Active Carbons Mark RAU)

Straw consumption by Russian enterprises decreased for many times. Simultaneously the volumes of corn production gradually increase leading to the increase of straw production (in our

Tab. 1. Characteristics of active carbons from straw

Tab. 1. Charakterystyka węgla aktywnego ze słomy

Initial straw	Apparent density, g/dm^3	Mass fraction of ash, %	Pore volume, cm^3/g			Adsorption capacity by:	
			Sum.	Pore sorpt.	micro	Iodine, %	MB, mg/g
Wheat	66.5	12.2	3.61	0.73	0.20	64	52
Oats	72.5	28.2	3.97	0.44	0.16	50	44
Rape	135	16.5	4.17	0.48	0.16	39	87

Tab. 2. Influence of active carbons on phytotoxicity of metsulphuron-methyl (Zinger, JV) on the example of sunflower

Tab. 2. Wpływ węgla aktywnego na fitotoksyczność metsulphuron-methyl (Zinger, JV) na przykładzie słonecznika

Variant	Average mass, g	% to control
Zinger, JV	1.1	73.2
Zinger, JV + AC from oats straw	3.9	4.9
Zinger, JV + AC from wheat straw	3.9	4.9
Zinger, JV + AC from pare straw	3.2	21.9
Zinger, JV + AC Grosafe	3.6	12.2
Contro (without herbicides)	4.1	-

Tab. 3. Characteristics of active carbons from nutshells and seeds of fruit trees

Tab. 3. Charakterystyka węgla aktywnego z pestek i nasion drzew owocowych

Seed of fruit tree	Packed density, g/dm^3	Abrasion strength, %	Mass fraction of ash, %	Pore volume, cm^3/g		Adsortive capacity by:	
				Sum.	micro	Iodine, %	MB, mg/g
Apricot	395	94.4	4.6	0.89	0.52	111	290
Peach	394	93.6	2.4	0.90	0.50	110	295
Coconut	410	90.3	2.7	0.85	0.57	110	270

country per year we have 80-100 mln. t. of only grain and cereal crops). Thus we meet the problem of the rational solution of post-harvest soil treatment and utilization of vegetable wastes as nowadays they are only incinerated or closed by soil.

For our research we chose straw of wheat, oats and rape. The methodology included the following. Straw was ground, loaded to a steel retort which was closed with a cover with connecting pipes and placed to an electrical oven giving nitrogen to the retort for creating an inert atmosphere. The retort was heated with the rate of temperature raise l–20°C/min to 450–500°C and held at the final temperature of carbonization for 30-60 min. After the end of the carbonization process the retort was transferred to the activation mode with water vapor at 850–870°C [2].

As we can see from Table 1, all the produced active carbons are characterized by the development of a summary pore volume ($V\Sigma$) and a considerable development of sorption volume (Ws), while the Volume of proper micropores (Vми) with the size 0.8 nm achieves 0.16–0.20 cm³/g, providing rather good values of adsorption capacity by iodine and methylene blue (MB).

You might define the efficiency of received AC directly during the soil detoxification from the remnants of applied herbicides [3]. The experiments were held in the laboratory of artificial climate (LAC) of GNU VNII of phytopathology RASHN (Golitsino, Moscow region). For sowing the test culture of sun flower we took pots with capacity 600 g of soil contaminated by herbicide Zinger in the dose, corresponding to 5g/ga, and put the dose of AC in the ration 100 kg per 1 ga. After 30 days and nights we estimated the average mass of the test plant. The results of the experiments are shown in Table 2.

We can see in Table 2 that suppression of growth towards the clean control in contaminated by herbicides soil (on the example of Zinger) with the usage of AC from wheat and oats straw makes only 4.9% while with world-known active carbon for soil mark Grosafe it makes 12.2%. It indicates that the efficiency of AC from straw is by 2.5 times higher than the used preparation for soil detoxification.

Tab. 4. Characteristics of active carbon produced by the method of chemical activation

Tab. 4. Charakterystyka węgla aktywnego wytwarzanego metodą aktywacji chemicznej

Index	Carbolin	OU-A by specification	UAF by specification	World level PHOM200 (England)
1. Feedstock	Sawdust	Birch coal	Coal	Coconut shell
2. Activity by iodine, %	235	70	70	103
3. Activity by MB, mg/g	604	225	190	246
4.Ash content, %	2.3	10.0	11.5	2.6
5. Content of compounds Fe^{3+}, %	0.09	0.2		0.04
6. Water content, %	0.3	10.0	5.0	5.6
7. Apparent density, g/dm^3	2112	-	-	320
8. Milling fineness (sieve residue 0.1 mm), %	18	5	5	
9.PH	3	4-6	8-9	9-11

Tab. 5. Results of trials of active carbon "Carbolin" against the requirements to AC used for drinking water treatment

Tab. 5. Wyniki prób węgla aktywnego "Carbolin" w zatosowaniu do wody pitnej

No. p/p	Name of indexes, units of measure	Requirements	Analyses data
1.	Adsorption activity by: -iodine, mg/g, not less methylene blue, mg/g, not less	880.0 220.0	1266.0 386.0
2.	Mass fraction: -water, %, not more -ash, % not more	10.0 10.0	3.9 2.35
3.	Mass fraction of water soluble ash, %, not more	2.0	0.5

Active carbons from nut shells and seeds from fruit trees (active carbons mark MeKS).

It is well known that the best active carbons from nutshells are AC produced from shells of coconuts. As such type of vegetable raw material is not available in Europe we took a similar type of packed vegetable raw material (seeds of peach and apricot) and produced pilot samples of these AC by the method of vapor-gas activation. In Table 3 you can see their physical-chemical and adsorption properties compared to active carbons on base of coconut shell mark GCN830 (Norit, Holland).

As we can see in Table 3 active carbons from fruit nuts (within the metering error 10%) are on'one level with active carbon on base of coconut. It opens broad prospects for creating on their base means of individual and collective protection of breath of filtering type as it is known that the best respirators are produced on basis of AC from coconut shell.

Active carbons from sawdust Active carbons mark "Carbolin"

Overall scope of wood waste in Russia makes about 150 mln m^3 a year while the part of sawdust and lignin does not make less than 50 mln m^3 a year. Scientists in the Northern Arctic Federal University (Arkhangelsk) developed AC mark "Carbolin" with specific surface 2500 m^2/g and adsorption capacity by iodine 200–300% and by methylene blue – up to 600 mg/g by the method of chemical activation of sawdust and lignin. Table 4 shows the characteristics of this active carbon compared to its industrial analogues.

As we can see from Table 4 active carbon "Carbolin" by its adsorption properties overcomes both Russian and world analogues by 2–3 times.

The powder form of "Carbolin" makes it indispensable in adsorbing processes of purifying drinking and waste water from organic pollutants. On basis of this trials of "Carbolin" were made against the requirements to active carbons for drinking water purification in OAO "NII Vodgeo" (Moscow) in the laboratory of deep water purification.

As we can see from the received data the main quality indexes of "Carboline" are considerably higher than the quality indexes of traditionally used in Russia active carbons OU-A, UAF, SPDK. Particularly, the activity by methylene blue is 1.5 times higher than for carbon OU-A and twice as high as for UAF, and it is 1.8 times higher than for carbons OU-A and UAF.

Taking into consideration that at present the purification with powered carbon is widely used

Tab. 6. Comparative characteristic of active spherical carbon adsorbent FAS with native and import AC

Tab. 6. Porównanie węgla aktywnego FAS z węglem imortowanym

Active carbon/apparent density (g/dm^3)	Summary pore volume, cm^3/g	Micropore volume, cm^3/g (cm^3/cm^3)	Mesopore volume, cm^3 /g; (cm^3/cm^3)	Mass fraction of ash, %	Abrasion strength, %
FAS/509	0.92	0.45 (0.23)	0.47 (0.24)	0.03	99.7
FAS/436	1.09	0.56 (0,24)	0.53 (0.23)	0.05	98.8
FAS/345	1.50	0.80 (0.28)	0.70 (0.24)	0.08	98.0
BAY-A/240	1.60	0.23 (0.07)	0.09 (0.02)	6.0	37.0
F-400/420	0.80	0.32(0.13)	0.12(0.05)	7.0	82.0

in water channels of Russia and world, the powered carbon "Carboline" with such high adsorption characteristics has excellent prospects of application.

Active carbons from hydrolyses products of corn stumps and sunflower husks (Active carbons mark FAS)

One of the most promising synthetic materials is furfural, the product of primary treatment of pentane containing vegetable raw material, above all corn stump and sunflower husk. Owing to the availability of the raw material and the high reactivity of furfural, it is one of the most wide spread products for producing various monomer and polymer materials in the world market. The availability of the vegetable raw material for many-ton production of furfural in the Russian Federation, possessing considerable and renewable feedstock, makes it possible to use it for creation manufacturing technologies of producing carbon adsorbents characterized by considerably improved physical-mechanical and adsorption capacities as compared to famous marks of active carbons.

The production of active carbon FAS included the following: furfural, sulfuric acid and active organic additives were mixed in a mixer with the volume not allowing the dwell time to exceed the time of its gelatinization. The composition partly gummed in the mixer went by gravity to the distributor, from its pipes in the form of sprays to the layer of hot oil where they depending on its viscosity were broken to the drops of the required size. The final resinification and cure of the product in the reactor took place during 15–18 sec. The separated from oil on the centrifuge product in the form of spherical grains with the size 2–3 mm was directed to thermal treatment and activation in rotary electrical furnaces at the temperature 850–870°C [4].

The characteristic of active carbons FAS of progressive activation is given in Table 6 in comparison with two AC of mass production: based on coal – F-400 (Calgon Carbon Corp., USA) and charcoal-raw product BAU-A (OAO "Sorbent", Russia).

Outstanding strength and adsorption characteristics of FAS, especially micropore volume per unit of volume (cm/cm3) by 2–3 times exceeding the similar values of industrially produced. AC in aggregate with almost zero ash content opens it the widest possibilities for solving the problems of protection from harmful exhausts of atmosphere, hydrosphere, Hthosphere and the man himself as a main object of biosphere. Thus, our researches for getting and applying active carbons on base of renewable vegetable raw material showed its huge potential for sorbents production preventing ecocide on the planet Earth.

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Odpady organiczne jako materiał do produkcji sorbentów węglowych

Powszechnie wiadomo że węgle aktywne są uniwersalnymi sorbentami pozwalające rozwiązać szereg zadań przemysłowych, problemów ochroną środowiska i zdrowia ludzkiego. Nową perspektywą jest produkowanie węgla aktywnego z odpadów roślinnych, w tym odpadów drzewnych, których ilość stale rośnie, a jedynym sposobem utylizacji jest spalanie.
W ostatnich latach opracowano trzy nowe technologie produkcji węgla aktywnego na bazie surowców roślinnych i pokazano perspektywy ich wykorzystania. Uzyskane sorbenty okazały się skuteczne przy oczyszczaniu spalin, do uzdatniania wody, poprawy jakości gleby.

Słowa kluczowe: węgiel aktywny, inżynieria środowiska, materiał roslinny, odpady drzewne