The Technology of *Helianthus Tuberosus* Agricultural Residues Processing to Obtain Activated Carbons

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Abstract

Today the issue of straw processing into fuel bricks is being widely discussed, for thermal capacity of such bricks made of straw of various agricultural crops is not lower, but even higher than that one of timber (timber produces usually up to 17,5–19,0 megajoule/kg). In order to obtain active carbons from straw of various oil Brassica crops (Camelina sativa) have been chosen as raw material. The technique was as follows.The straw was milled, loaded into a steel retort, which was capped and placed in the electric furnace, feeding nitrogen into the vessel to create an inert atmosphere. The retort was heated at a rate of temperature rise 1–20°C/min to 450–500°C and maintained at the final carbonization temperature for 30–60 min. After completing the process of carbonization the retort was switched to the mode of steam activation at 850–870 °C. Powder activated carbons, obtained from Camelina sativa, false flax, barley and wheat straw according to this technology has a product yield of 5.7%. The obtained powder activated carbon was analyzed in accordance with the accepted state standards and the following characteristics have been determined: Ac = 15.6% by weight; Δ = 140 g/dm3; VΣ = 2.43 cm^3/g; Ws = 0.69 cm^3/g, the adsorption capacity for iodine and methylene blue (MB) was 43 and 82 mg/g. As a result, during activation process a vast sorption space Wsis being developed, which leads to a high iodine adsorption. The active carbons adsorption isotherm of nitrogen, measured on the device ASAP- 2020, made possible calculating the parameters of its microporous structure: micropore volume (Vmi) – 0.135 cm^3/g, micropore size (full width of the gap) – 1.66 nm the total pore surface area (Sud – 380 m^2/ g), the adsorption energy Ea – 19.8 kJ/mol. We have developed and studied polyfunctional, environmentally safe (nano) chips based on oligo-, polysaccharides and activated carbon derivatives, obtained from waste vegetable matter (straw of various oil Brassica crops). Their influence on growth, development, seed yield and quality of various crops (corn crops, legumes, oil crops and etc.) has been determined. Extending target properties of various agricultural (nano)polymerous materials provides optimal level of gradual consumption of physiologically active substances, decreasing chemical load and increasing plant resistance to unfavorable environmental factors.

Keywords: active carbon, adsorption, characteristics, agricultural plant residues (straw), oligo- polysaccharides, (nano) chips, physiologically active substances

Introduction

Progressive Territories have enormous resources of various carbon containing raw materials, which application allows of obtaining different unique activated carbons with various physical-chemical properties, porous structure, which can be used in different spheres of human activity (agriculture, medicine, food production and so on) (Mukhin, 2003, 2012; Voropaeva, 2014a).

Activated carbons offer such advantages as universal sorptive power, high absorbing capacity, selective absorption of organic toxicants, easy-to-use preparation form (grains, powder), hydrophobic behavior and low prices, all these are very important when solving various practical and environmental problems in the sphere of agriculture.

Today the issue of straw processing into fuel bricks is being widely discussed, for thermal capacity of such bricks made of straw of various agricultural crops is not lower, but even higher than that one of timber (timber produces usually up to 17,5–19,0 megajoule/kg) (Voropaeva, 2014b).

Considering the fact that application of straw of various agricultural residues as litter material, animal food or as some additional ingredients to this, as heat-insulating material or for some other purposes in nowadays households (as roofing material and sun-dried bricks or cobs) has been dramatically reduced due to abrupt livestock number reduction, new ways of livestock keeping, new technologies in agriculture and cattle breeding in general, one can understand that after-harvest soil treatment and residues management are the problems to be solved today, new approaches are needed here. Straw processing into pressed briquettes allows of solving various problems -from raw material storage not being dependent on the season and its transportation to automatization of the process of loading materials into furnace plants.

However, taking into consideration that, unlike livestock farming, world grain production displays a tendency to increase (due to the probable and expected food shortage when providing the whole world with food), and, accordingly, straw production growth takes place (mass of cereal crops accumulated straw only amounts in Russian Federation to 80–100 million tones, besides, this straw is usually burnt or ploughed into the soil), every new approach to agricultural residue processing in order to obtain various useful, valuable products is important from the scientific and practical point of view.

It is widely known that activated carbon powder is, as a rule, obtained by grinding grained activated carbon, so it makes sense to obtain such activated carbons from various agricultural plant residues to exclude extra power inputs.

To make carbon porous structure optimal for absorption of various toxicants, it is important to provide not only the necessary carbonisation temperature, but also securely fixed hold-up time with the fixed final temperature for formed carbon crystal structure fixation– the matrix for micropore size formation. Besides, the activation temperature, influencing micropore sizes, provides prevailing of micropores of given sizes. By varying steam flow rate per kilo of carbonised product, one may get the necessary size or capacity of transferring pores, thus providing efficient adsorption kinetics (Mukhin, 2012).

The goal of our researches is to develop the technologies of multipurpose activated carbon production from agricultural plant residues of cereal and oil crops.

Experimental

Activated carbons obtained from straw. In order to obtain active carbons (RAC) from straw of various oil Brassica crops (Camelina sativa) have been chosen as raw material. The technique was as follows.

The straw was milled, loaded into a steel retort, which was capped and placed in the electric furnace, feeding nitrogen into the vessel to create an inert atmosphere. The retort was heated at a rate of temperature rise 1–20°C/min to 450–500°C and maintained at the final carbonization temperature for 30–60 min. After completing the process of carbonization the retort was switched to the mode of steam activation at 850–870°C.

Testing of active carbons from straw. The effectiveness of active carbons for the detoxification

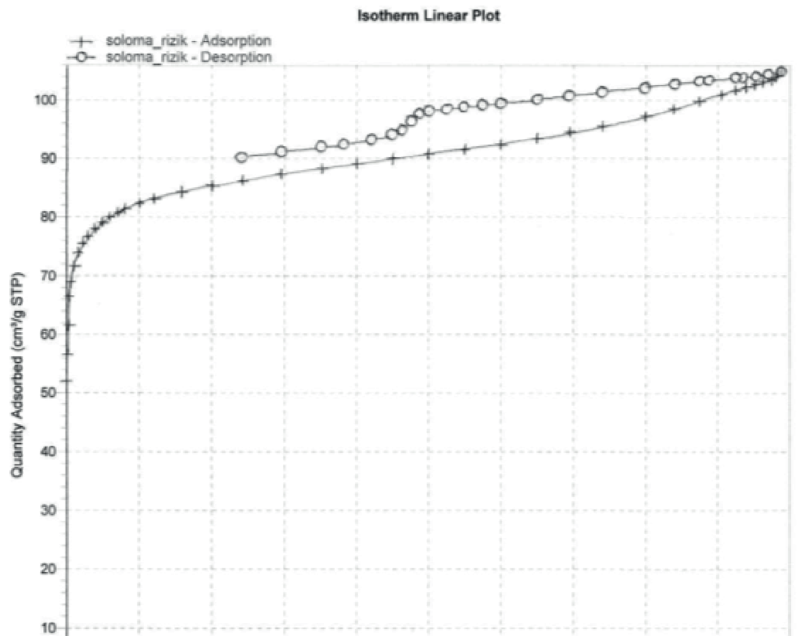

Fig. 1. Adsorption and desorption isotherm curves of false flax straw (Camelina sativa) activated carbons

Rys. 1. Izotermy adsorpcji i desorpcji węgli aktywnych ze słomy lnianej (Camelina sativa)

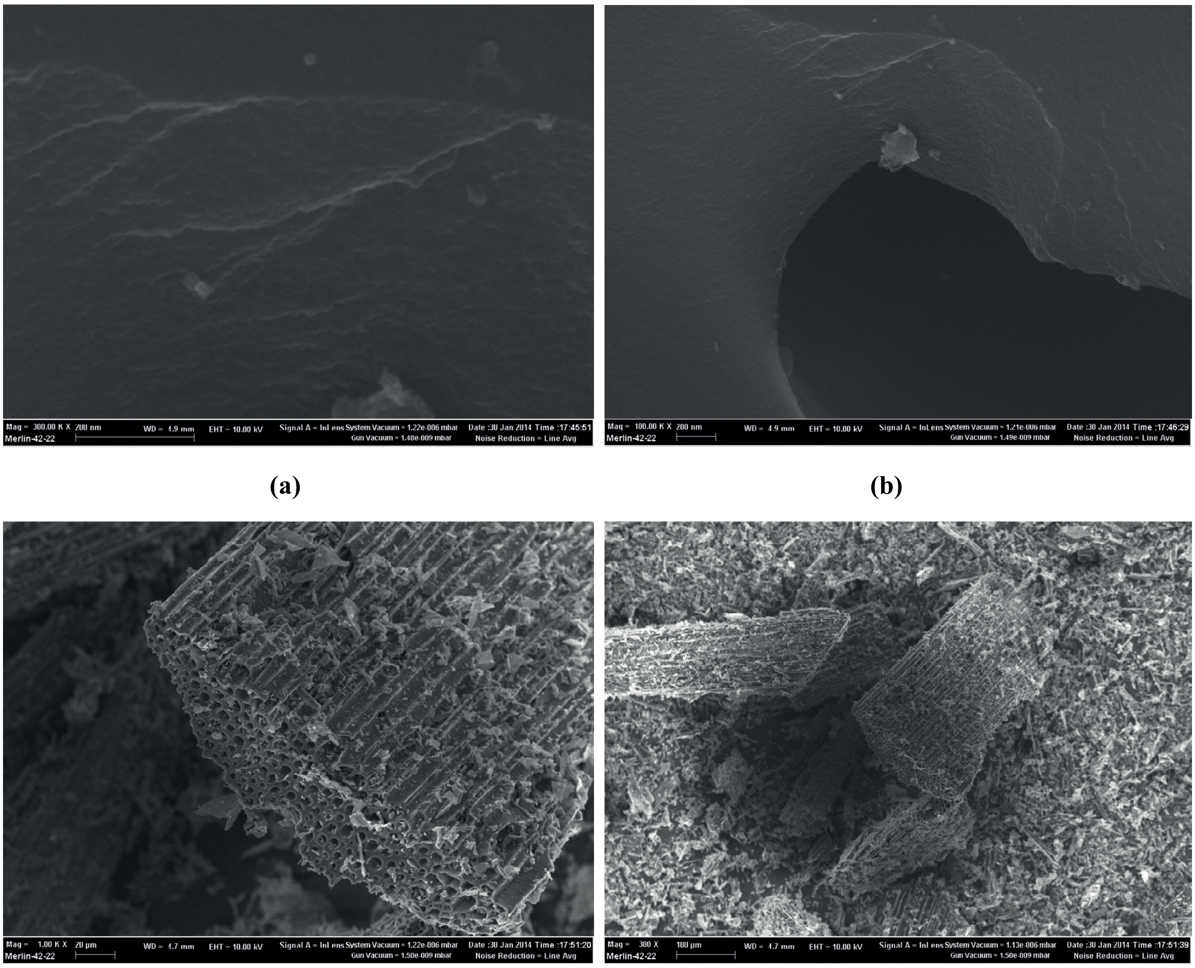

Fig. 2. Electronic micrographs of powder activated carbon of false flax straw (Camelina sativa) with different resolution (a – 300,00 Kx 200 nm, b – 100,00 Kx 200 nm, c – 1,00 Kx 20 μm, d – 300,00 Kx100 μm)

Rys. 2. Analiza SEM węgla aktywnego ze słomy lnianej (Camelina sativa) dla róznych rozdzielczości (a – 300,00 Kx 200 nm, b – 100,00 Kx 200 nm, c – 1,00 Kx 20 μm, d – 300,00 Kx100 μm)

of soil from residues of applied herbicide has been evaluated (Spiridonov, 2015). The experiments were conducted in the laboratory of artificial climate (LAC) of the State Research Institute of Phytopathology RAAS (Golitsino, Moscow region). In order to sowing sunflower test culture, the pots with a capacity of 600 g of soil were used. The samples of soil were contaminated with the Singer herbicide in a dose corresponding to 5 g/ha. The tested active carbons were injected in a dose of 100 kg per 1 ha. After 30 days the average weight of the test plant was evaluated.

Standard test methods, including evaluation of ash content , bulk density , strength to abrasion , adsorption capacity for iodine and methylene blue (MB) have been used to characterize obtained activated carbon samples. Total pore volume (V_{Σ}) was determined by adsorption of water. Sorption volume (W_S), micropore (V_{mi}) and mesopore volumes (V_{meso}) have been determined from nitrogen-sorption isotherm by using the ASAP 2020 device (Micromeritics, USA) (Mukhin, 2003).

Straw carbonization in nitrogen atmosphere according to the method, described in (Mukhin, 2012), has been studied, process variable influence on carbonator properties and yield has been determined. Optimal process conditions have been detected (isothermal exposure temperature and duration), they allow of obtaining microporous carbon matrixes with the definite parameters of transferring pores. Physical activation of the obtained carbons with water steam has been studied. Process variable influence on the properties and yield of activating agents has been determined. Optimal process conditions, allowing to obtain activated carbons with the given micropore specific surface and capacity, have been detected.

Results and discussion

Powder activated carbons, obtained from Camelina sativa, false flax, barley and wheat straw according to this technology has a product yield of 5.7%. The obtained powder activated carbon was analyzed in accordance with the accepted state standards and the following characteristics have been determined: Ac = 15.6% by weight; Δ = 140 g/dm^3; V_Σ = 2.43 cm^3/g; W_s = 0.69 cm^3/g, the adsorption capacity for iodine and methylene blue (MB) was 43 and 82 mg/g. As a result, during activation process a vast sorption space Ws is being developed, which leads to a high iodine adsorption. Taking into consideration the values of the adsorption activity of iodine and methylene blue, these coals are fully applicable for wastewater treatment and even perhaps for drinking water purification by "carbonning" (coal slurry injection into the reaction chamber) at water stations.

The RAC adsorption isotherm of nitrogen (see Figure 1), measured on the device ASAP-2020, made possible calculating the parameters of its microporous structure: micropore volume (Vmi) – 0.135 cm^3/g, micropore size (full width of the gap) – 1.66 nm the total pore surface area (Sud – 380 m^2/ g), the adsorption energy Ea – 19.8 kJ/mol.

The porous structure parameters of AC of false flax determined from the adsorption isotherm fully correspond to the parameters of the domestic industrial activated carbons (see Figure 2 a, b, c, d).

This means that they can be effectively used in various carbon absorbing industrial processes wherein powdered activated carbons are used.

These carbons have a very high polyphenol sorptive capacity, which is 3.0 higher than that one known of activated carbons. Obtained sorbent agents can be used as soil detoxicants, helping to get rid of various residual quantities of pesticides and mixed fodder – from dangerous xenobiotics. They can be used, for example, being parts of (nano) chips, as various physical property carriers during pre-sowing seed treatment, they can be also used to solve other agricultural problems.

We have developed (nano) chips and studied their physical-chemical and structural properties, their efficiency for various crops cultivation technologies as the chips based on (nano) systems, consisting of activated carbons, modified natural minerals with high absorptive capacity, oligo-, polysaccharides and their derivatives (Karpachev, 2014).

The conducted laboratory tests have shown that rape, winter cress and mustard (as standard crops) pre-sowing seed treatment with activated carbons as highly efficient sorbents of the following brands VCK, VCK-400, AG-3, BAU-A, FAS, UBF and (RAU sorbent has been obtained, for example, from (Camelina sativa straw) facilitated seed germination. The number of seeds germinated during the first day increased by 4.6–33.9% depending on the physical-chemical properties of the sorbents studied. Germination energy increased by 2.8%, laboratory germination by 4.0%, shoots length by 5.4–35.4 mm, accumulated mass by 5.9%–29.0% in comparison to the control variant (with the seeds not treated) (Spiridonov, 2015).

Adding activated carbons of the following brands VSK, VSK-400, AG-3, BAU-A, FAS, UBF, FAU into (nano) chips gave a major boost to seed germination process (the number of seeds germinated during the first day increased by 25.7–51.3%, germination energy increased by 3.0%, laboratory germination by 4.9%, seedling lengths by 5.7–39.6 mm, maximum mass accumulation by 6.9–35.5% in comparison to the control variant (when the seeds have not been treated).

Conclusions

Thus, powder carbon absorbents from raw plant material residues – the straw of various agricultural crops, have been obtained, the complex of physical – chemical and structural properties, has been studied, their sorptive capacity has been estimated, we have also detected their efficiency for pre-sowing seed treatment of oil and cabbage crops.

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Zastosowanie technologii Helianthus tuberosus *do przetwarzania odpadów rolnych w celu uzyskania węgla aktywnego*

*Obecnie na szeroką skalę prowadzone są prace dotyczące przetwarzania słomy na brykiety opałowe. Wartość opałowa brykietów wyprodukowanych ze słomy różnych rodzajów zbóż jest nie niższa, a nawet wyższa od tych wyprodukowanych z drewna (drewno zazwyczaj wytwarza do 17,5–19,0 megadżuli/kg). W celu otrzymania aktywnego węgla ze słomy, jako surowiec wybrano odmiany roślin oleistych z gatunku kapusty Brassica (*Camelina sativa*). Metoda badawcza była następująca – słomę zmielono i umieszczono w stalowej retorcie, która później została uszczelniona i włożona do pieca elektrycznego, do naczynia podano azot by wytworzyć atmosferę inertną. Retortę podgrzano z szybkością 1–20°C/min. do temperatury 450–500°C, temperaturę utrzymano na poziomie docelowej karbonizacji przez 30–60 minut. Po zakończeniu procesu karbonizacji, retortę utrzymano w trybie aktywacji pary w temperaturze 850–870°C. Węgiel aktywowany uzyskany ze słomy lnicznika siewnego, lnianki, żyta, jęczmienia i pszenicy dzięki powyższej metodzie osiągnął wydajność 5,7%. Następnie węgiel aktywowanego przeanalizowano wg akceptowanych obecnie standardów i określono następujące właściwości: Ac = 15,6% wg wagi; Δ = 140 g/dm^3; VΣ = 2.43 cm^3/g; Ws = 0.69 cm^3/g, zdolność adsorpcji jodu i błękitu metylenowego wyniosła odpowiednio 43 oraz 82 mg/g. W następstwie, podczas procesu aktywacji rozwinęła się rozległa powierzchnia sorpcyjna Ws, co doprowadziło do wysokiej adsorpcji jodu. Izotermy adsorpcji azotu na węglu aktywnym, zmierzona przy użyciu sprzętu ASAP – 2020, umożliwiła wyliczenie parametrów struktury mikroporowej: mikroporowa objętość (Vmi) – 0,135 cm^3/g, rozmiar mikropory – 1,66nm, powierzchnia całkowitą pory (Sud – 380m^2/g), energię adsorpcji Ea – 19,8 kJ/mol. Opracowano i zbadano wielofunkcyjne, bezpieczne dla środowiska (nano) wióry składające się z oligo- i polisacharydów oraz derywatów węgla aktywowanego, uzyskanych z odpadów roslinnych (słoma różnych odmian roślin oleistych Brassica). Ustalono ich wpływ na wzrost, rozwój, wydajność ziarna i jakość wielu upraw (kukurydzy, roślin strączkowych, roślin oleistych itd.).*

Słowa kluczowe: węgiel aktywny, adsorpcja, charakterystyka, odpady roślin rolniczych (słoma), oligo-polisacharydy, (nano) czipy, substancje aktywne fizjologicznie