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Refuse-derived fuel waste conversion to carbon adsorbent

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Refuse-derived fuel (RDF) fuel can be produced from various types of waste, consisting of combustible components, like paper, polypropylene, polystyrene, polyethylene, bitumen waterproofing, nylon and other waste materials. RDF can be also produced from used tyres and biomass waste. In this work nanoporous carbons are prepared from RDF from waste tarpaulin made of bitumen. First the precursor sample was subjected to oxidation at a temperature of 250-300 °C with constant stirring and feeding of oxidant. Second step is pyrolysis at 600 °C, followed by subsequent hydro-pyrolysis at 750 °C. The synthesized carbon was characterized by N_2 physisorption at -196 °C, elemental analysis, etc. The results show that nanoporous carbon from RDF is characterized by high surface area around 700m^2 and significant content of micro- and mesopores. The adsorption of dyes from water by obtained nanoporous carbon was studied, the change in the concentration of dye in the water was monitored by UV-VIS spectrophotometer. The results suggest that obtained nanoporous carbon is suitable for application as adsorbent of organic and inorganic pollutants. Liquid products and gases are also obtained.

Key words: RDF fuel; waste material; nanoporous carbon; adsorbent

INTRODUCTION

RDF can be produced from varios types of waste, such as municipal waste and industrial waste, and its composition is a mixture of materials with higher flammability (paper, non-recyclable and not containing Cl, F plastics) compared to the components in the total waste stream. RDF fuel is used to produce electricity and heat in various types of equipment and cement industry. In some European countries there are strict standards, culture of recycling, collection system and better screening of well-combustible components for production of RDF [1, 2]. However, in most countries they are difficult to recycle due to limited technology and available facilities, which leads to severe pollution of the soil, air and water, due to the content of not so well combustible materials, pollutants such as carbon monoxide, sulfur and nitrogen oxides, heavy metals, polycyclic compounds, etc. [1, 2].

Carbon adsorbents are often synthesized from precursors based on expensive and exhaustible fossil fuels, but they can also be readily obtained from a variety of cheap and alternative precursors - coal, biomass, polymer waste [3-15].

Nowadays microplastics and nanoplastics have become pollutants of global importance, due their slow biodegradation. They are small enough to be ingested by and accumulated in algae, plants and animals, and they could cross some biological barriers. In the last 60 years global plastic waste is around 6000 million tonnes, and 80% are accumulated in urban teritories, beaches, landfills, aquatic environment, etc. [16].

In the last years, the scientific interest has focused on the development of carbon synthesis methods based on mixtures of organic substances - liquid products from thermal treatment of biomass, furfural, coal tar, polymer waste products, etc. [11-13].

Methods of synthesis used have additional contribution for waste utilization. Obtained materials found environmental application as adsorbents and catalysts. The experimental data obtained on the processes occurring during the thermo-catalytic treatment of some precursors show that the direction of this study is promising, with potential for further development and for promising results [11-13].

Various technologies for the production of polymers have led to the production of a large number of by-products, but most of these polymeric waste products have not found suitable application so far. Due to their affordability and low cost, polymers and polymer waste products are suitable

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precursors for the production of nanoporous carbon materials. Thermochemical conversion of polymer waste products is an appropriate way of producing energy as well as carbon with good adsorption properties and low content of mineral impurities. On the other hand, the current paper will be focused on the treatment of RDF fuel waste in order to obtain adsorbents for the treatment of industrial and waste water from various pollutants.

Wastewater can be classed as sanitary, commercial, industrial, agricultural or surface wastewater. The sources of industrial wastewater are cement, pharmaceutical, food, textile, pulp paper, rubber, leather, cosmetics, plastic industries, fertilizers, etc. 20% of industrial water pollution is result of textile dyeing and treatment. Dyes produced by the textile, printing and paper industries are a source of pollution of rivers and waterways. 700 000 tons of dyes used during the manufacturing of textile products is released into the environment worldwide annually [17, 18]. In high concentrations synthetic dyes have toxic, carcinogenic, mutagenic and teratogenic effects on humans, microorganisms, fish, etc. [17, 18].

The main aim is to utilize the RDF fuel obtained by processing it into liquid and gas products to be used as energy sources and a solid product /carbon adsorbent/ to be used for purification of water and air from industrial and domestic pollutants. An additional contribution is the utilization of waste products from the industry. The relationship between the physicochemical properties of the adsorbents obtained and their adsorption capacity against certain compounds hazardous to human health will be investigated. The most suitable raw materials, surface modification methods and processing conditions will be found to obtain effective carbon adsorbents to remove dyes (methyl orange and bromthymol blue) from water.

MATERIAL AND METHODS

Linoleum material is finely chopped to a fraction suitable for its processing, as the size of the pieces varies from 2 to 5 mm. The material is subjected to following procedures:

Thermal oxidation (Fig. 1) - the prepared fraction of bitumen waterproofing is poured into the reactor - 2, with constant stirring by a stirrer - 1, heating at temperature 250-300 °C for 30 min. and feeding oxidizer (in our case - conc. H_2SO_4, added by drops). The gases are captured by the drexel - 3.The oxidation and heat treatment of RDF with different oxidants affects the composition to a very large extent, the resulting product has a very different composition from that of the starting product.

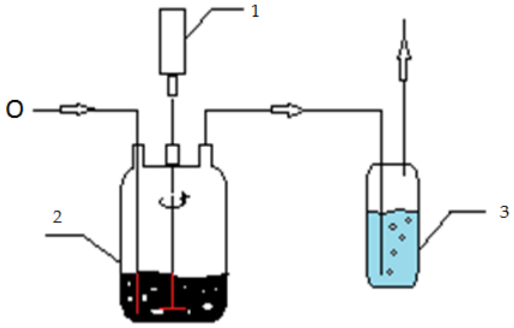

Fig. 1. Scheme of the thermal oxidation process.(1- mechanical stirrer, 2- stainless steel, 3- drexel).

The next stage is heat treatment in an atmosphere of its own volatiles (Fig. 2).The oxidized RDF is placed in the reactor - 2, after heating at 600 °C for 1h in the furnace – 1, the volatile substances are separated, the liquids are collected in a receiver – 5. The gases bubble in the drexel - 7, which contains a basic solution for capturing acid gases, the remaining amount flows through gas meter - 8, and could be used for fuel.

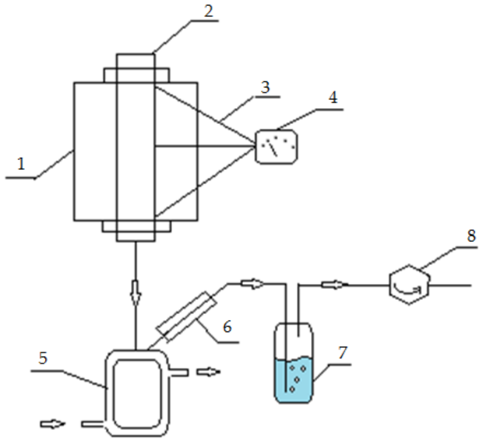

Fig. 2. Heat treatment (1 - furnace, 2 - reactor, 3 - thermocouples, 4 - thermal controller, 5-receiver, 6-condenser, 7-drexel, 8-gas meter).

The third stage is hydropyrolysis in a stainless steel reactor (Fig. 3). A steam generator -1, is added to the installation, as the atmosphere of water vapor for 1h at 750 °C forms new pores and expands the already formed ones.

Micro-meso-porous structure of the carbon adsorbent is formed.

The textural properties of adsorbents were measured on Quantachrome NOVA 1200e USA (model e-25, 2014) using N_2 adsorption-desorption at −196 °C. Prior to measurement, the samples were degassed at 300 °C for 4 h to remove the presence of impurities and/or moisture.

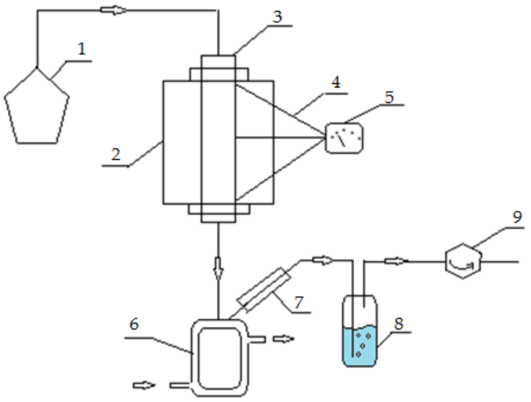

Fig. 3. Hydropyrolysis (1 – steam generator, 2 - furnace, 3 - reactor, 4 - thermocouples, 5 - thermalcontroller, 6 - receiver, 7 - condenser, 8 - drexel, 9 - gas meter).

The elemental analysis was performed on ELEMENTAR analyser, model VarioMacroCube (2018), to determine C, H, N, S. The dye concentration is determined on UV-VIS spectrophotometer Spectroquant Pharo 300 Merck (2008).

RESULTS AND DISCUSSION

Moisture was determined after drying in an oven at 120 °C to constant weight, the ash content is the remainder after 10 min at 850 °C. Technical analyses, material balance and elemental analysis are presented in Tables 1-3, respectively.

Table 1. Technical analysis of activated carbon from RDF.

W, wt% (moisture content)	**A, wt%** (ash content)
0.5	30

Table 2. Material balance of the products of pyrolysis of activated carbon from RDF.

Solid product wt.%	**Liquid products wt %**	**Gas + losses wt%**
49.2	17.6	34.2

The atomic ratio of carbon to hydrogen is 1.75. The result gives an idea of the degree of carbonization (predominant amount of carbon) and aromaticity. Data show the presence of significant amounts of polycyclic aromatic compounds, including condensed aromatic compounds. This proves the successful synthesis of the carbon adsorbent.

Nitrogen physisorption (−196 °C) isotherm and textural parameters of the activated carbon from RDF are presented in Fig. 4 and Table 4. The results show that nanoporous carbon from RDF is characterized by high surface area and significant content of micro- and mesopores. The analysis clearly shows that the micropores predominate, which proves the nanoporous structure of the adsorbent. The results suggest that obtained nanoporous carbon is suitable for application as adsorbent of organic and inorganic pollutants.

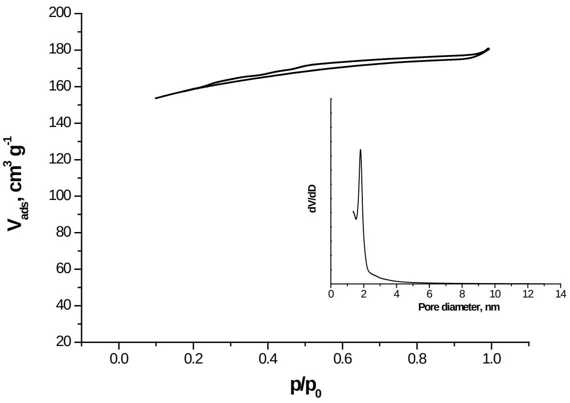

Fig. 4. Nitrogen physisorption (−196 °C) isotherm of the activated carbon from RDF.

Determination of adsorption capacity is performed as follows. Solutions of methyl orange (MO) with a concentration of 0.5 to 10 mg / L and bromothymol blue (BTB) with concentrations of 10 to 30 mg / L were prepared, the adsorptions were carried out for periods of 10, 30 and 60 min.

The adsorption of methyl orange gave the best result (87 mg/g maximum adsorption capacity) at a concentration of 1 mg /L for a period of 10 minutes, whereas for bromothymol blue adsorption the best result (87 mg/g maximum adsorption capacity) was demonstrated at 10 mg /L for 60 minutes.

Table 3. Elemental analysis of activated carbon from RDF.

Sample	**C, wt. %**	**C, at. %**	**H, wt. %**	**H, at. %**	**N, wt. %**	**N, at. %**	**S, wt. %**	**S, at. %**
Activated carbon from RDF	47.1	3.93	2.25	2.25	4.2	0.3	2.3	0.07

Table 4. Technical analysis of activated carbon from RDF.

Sample	**BET specific surface S_{BET}, m^2/g**	**Total pore volume [a] V_{total}, cm^3/g**	**Micropore volume [b] V_{micro}, cm^3/g**	**Mesoporous volume [c], cm^3/g**
Activated carbon from RDF	650	0.25	0.22	0.02

[a] calculated at $p/p^0 = 0.99$; [b, c] calculated by the Dubinin-Radushkevich method

CONCLUSION

Nanoporous carbons are successfully synthesized from RDF from waste tarpaulin made of bitumen. The synthesized carbon is characterized by N_2 physisorption at -196 °C, elemental analysis, etc. The results show that nanoporous carbon from RDF is characterized by high surface area and significant content of micro- and mesopores. The adsorption properties of obtained carbon material towards dyes in water was studied using UV-VIS spectrophotometry. The results suggest that obtained nanoporous carbon is suitable for application as adsorbent of organic and inorganic pollutants.

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