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Conversion of polyolefin wax to carbon adsorbents by thermooxidation treatment

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Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

Carbon adsorbents with different properties were obtained from furfural and mixture of furfural and polymer waste (polyolefine wax) with different activation reagents and different conditions of treatment. The carbons obtained have insignificant ash content. It was determined, that pore volume, pore size distribution and the chemical character of the surface of the carbon adsorbents depend on the selected activation reagents and temperature of treatment. The IR spectra and Boehm method show that various oxygen-containing groups with acidic (carboxylic, carboxylic in lactone-like bonding, phenolic, hydroxyl and carbonyl groups) and basic character are present on the carbon surface. Our investigations reveal that on the base of polymer waste, different activated carbons were obtained, and they could be used as effective adsorbents for removal of toxic metal and organic pollutants.

Key words: adsorbents, polymer waste, furfural, surface characterization

INTRODUCTION

Many materials in everyday life are produced from plastics and other petroleum derivatives. Plastics have unique properties and strong chemical bonds, which are not biodegradable, thus contributing to environmental pollution after use. Utilization of plastic waste can be performed by using of various methods of thermal destruction including thermal cracking (pyrolysis), catalytic cracking, gasification and hydrocracking. Pyrolysis is often used as effective method to convert waste plastic into useful products - fuels, lubricant oils, different chemicals, etc.

There are a lot of investigations dedicated on synthesis of carbon materials from polymer materials – polymers, polymer resins and polymer waste [1-21]. Thermoplastic polymers (polyethylene, polypropylene, polyvinyl chloride, polyamide, polystyrene, polyacrylic, etc.) and thermosetting resins /epoxy resins, formaldehyde resins, melamine resin, etc./ also are suitable precursors. Polyvinyl chloride (PVC) as thermoplastic polymer is suitable precursor for porous activated carbons, synthesized by oxidation and subsequent procedures of carbonization and activation [1-6]. PVC has melting temperature of 160°C (but around 140°C it starts to decompose), and when heating is first decomposed to hydrogen chloride and unsaturated polymers, which decompose later to other low-molecular products [7,8]. Some authors report about preparation of polystyrene-based activated carbon [9,10]. There are some papers concerning polyethylene terephthalate PET utilization [11-14], however the methods used are complicated, due to the fact that the material is hardly degradable. Some authors produced activated carbon (AC) from polyurethane [15]. Others [11,16] used polyacrylonitril (PAN) fibres to obtain porous carbon. There are also some investigations dedicated to utilization of paper [11] and automobile tyres [17,18].

Polyethylene is also potential precursor. The bags used in grocery stores to carry foods and goods are made of high-density polyethylene (HDPE), and the bags usually used in department and fashion stores are made of low-density polyethylene (LDPE). Polyethylene is a product of petroleum, a non-renewable resource which takes many centuries to break down when put in a landfill. The composition of products from the pyrolysis of pure polyethylene was studied by several researchers [19-21]. Polyolefin wax ($(CH_2)_nH_2$, where n ranges between about 50 and 100) is a by-product from polyethylene production, and it is formed as a result of side reactions, i.e. polyethylene cracking at high temperatures (>400°C).

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The aim of this study is to obtain porous activated carbon using polyolefin wax as precursor.

EXPERIMENTAL

The polyolefin wax sample (waste product of polyethylene production at low pressure; from Burgas petroleum plant, Bulgaria) has melting point 115°C, average molecular mass of 1100. When heating in air at 360°C it decomposes (without solid residue) to low-molecular products, which evaporate.

200 g polyolefin wax (POW) was heated up to 115°C until melting. Concentrated sulfuric acid was added by drops during continuous stirring, and the temperature was increased up to 160°C. The obtained solid product was washed with water, dried at 150°C and carbonized at 600°C.

POW carbonizate was subjected to oxidative thermal treatment at 400°C for 1h in a quartz boat in a horizontal tube furnace in a flow of air. The obtained sample is denoted POW-OC.

POW carbonizate was subjected to water steam activation at 800°C for 1 h. The obtained solid product is denoted as POW-AC.

Mixture of 120 g POW and 80 g furfural was heated up to 115°C until melting. The furfural is added for intensification of polymerization and polycondensation, thus decreasing the expense of H_2SO_4. Conc. H_2SO_4 acid was added by drops during continuous stirring, and the temperature was increased up to 160°C. The obtained solid product was washed with water, and then dried at 150°C and carbonized at 600°C. The carbonizate was subjected to water steam activation at 800°C for 1 h. The obtained solid product is denoted as FPOW-AC.

FTIR experiments were performed by spectrometer IFS 113V using pellets with KBr. Textural characterization was carried out by measuring the N_2 adsorption isotherms at -196°C using Micrometrics ASAP 2010. Prior to the adsorption measurements the samples were outgassed in situ under vacuum at 120°C overnight, to remove any adsorbed moisture and gases.

The isotherms were used to calculate specific surface area S_{BET}, and total pore volume V_t, assuming a slit-shaped pore geometry [22].

The content of oxygen-containing functional groups with acidic character on the carbon surface was determined applying the Boehm method by neutralization with bases of increasing strength: $NaHCO_3$, Na_2CO_3, NaOH, and sodium ethoxide [23]. About 0.5 g of the sample was put in contact with 100 mL of 0.05 N base solution in sealed flasks. The suspensions were shaken at least 16 h, and then filtered. The excess of base remaining in the solution was determined from back-titration after adding an excess of standard HCl solution. It was assumed that $NaHCO_3$ was capable of neutrallizing all carboxylic groups, Na_2CO_3-carboxylic and lactonic groups, NaOH-carboxylic, lactonic and phenolic groups, and sodium ethoxide was assumed to neutralize all acidic groups. The total number of basic sites was determined with 0.05 N HCl [24]. The procedure is the same as above mentioned, as back-titration of the excess of HCl was performed using titration with 0.05 N NaOH solution.

Carlo Erba 1106 combustion elemental analyzer was used for C and H. Sulfur content was determined by Eshka method. Oxygen content was determined by the difference.

RESULTS AND DISCUSSION

The results from elemental analysis of the obtained samples are presented on Table 1.

Table 1. Chemical characterization.

Sample	Ash^{mf} wt. %	C^a wt. %	H^a wt. %	S^b wt. %	O^c wt. %
POW carbonizate	0.10	87.1	3.7	1.0	8.2
POW-OC	0.10	80.2	3.7	0.9	16.7
POW-AC	0.11	87.4	3.5	0.5	8.6
FPOW-AC	0.12	88.6	1.1	0.3	10.0

^{mf}moisture free sample; ^{a}data from combustion elemental analyzer; ^{b}data from Eshka method; ^{c}determined by the difference.

Elemental analysis shows that activated samples have higher carbon content due to the higher temperature treatment and structure changes of the sample. The oxidation with air leads to significant increase of oxygen content.

The results from N_2 adsorption isotherms (Fig. 1) show that FPOW-AC is characterized with an opening of the knee at low relative pressures. This indicates the development of mesoporosity and a widening of the microporosity in these samples. The surface characteristics are presented in Table 2. The results show that FPOW-AC is distinguished by very high surface area and micropore volume, while POW-AC and POW-OC have considerable amount of micropores and moderate surface area. The oxygen-containing functional groups on the surface of carbons are a very important specific characteristic. The experimental data from Boehm titration (Table 3) show that various oxygen-containing groups (carboxyl groups, carboxyl groups in lactone-like binding, phenolic hydroxyl and carbonyl groups) of acidic and basic character, and with different chemical properties, are present on the surface of the samples. Basic groups are not detectable in the oxidized samples. These results are confirmed by the elemental analysis.

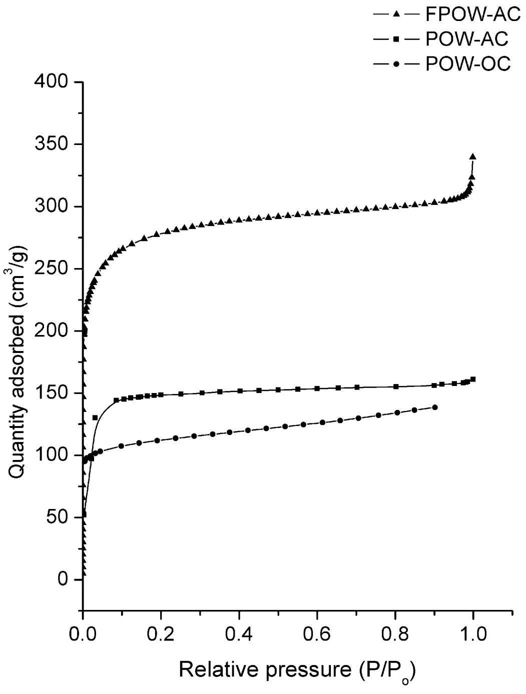

Fig. 1. N_2 adsorption isotherm of investigated carbon samples.

IR spectra of the samples are presented on Fig. 2. Stretch vibrations of associated –OH groups (3400–3230 cm^{-1}) were detected.

The absorption is a consequence of the presence of OH groups in the precursor. The bands at 3000-2800 cm^{-1} are due to aliphatic stretching vibrations. C-H stretching vibrations in the region of 3000–2800 cm^{-1} and C-H deformation vibrations in the region 1470–1350 cm^{-1} are related to aliphatic structures. The band at 1704 cm^{-1} could be related to the stretching of C=O in linear aliphatic aldehydes, ketones and carboxyls [25]. The bands around 1600 cm^{-1} cannot be interpreted unequivocally. They could be due to: 1) aromatic ring stretching coupled to highly conjugated carbonyl groups (C=O); 2) stretch vibrations of C=C bonds in aromatic structures; 3) OH groups. The bands in the region of 1360–1150 cm^{-1} are due to C–O in complex ethers and ring structures. The IR spectroscopy results confirm the presence of oxygen-containing groups on the surface.

Table 3. Chemical characterization.

Sample	$NaHCO_3$	Na_2CO_3	NaOH	NaOEt	Basic groups
POW carbonizate	0.12	0.250	0.340	0.900	0.120
POW-OC	0.69	0.39	2.51	3.510	BDL
POW-AC	BDL	0.100	0.220	2.100	0.600
FPOW-AC	BDL	0.135	0.28	2.334	0.552

BDL-below detection limit.

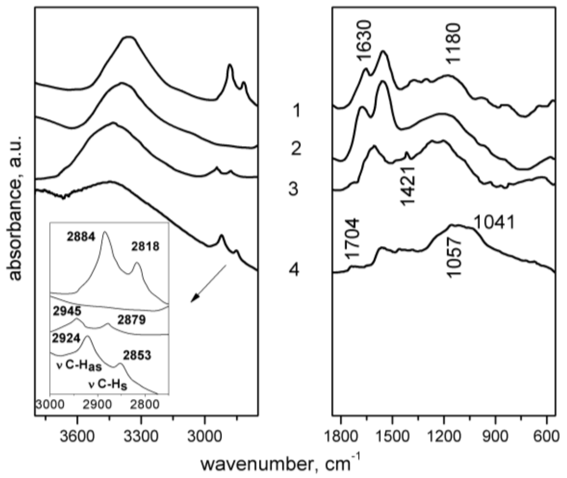

Fig. 2. IR spectra of the investigated samples: 1- POW carbonizate; 2 - POW-OC; 3 - FPOW-AC; 4 - POW-AC.

In summary, oxidized carbons have different properties (hydrophilic character, selective ion-exchange capacity, etc.) than water vapor activated carbons, due to the chemical nature of the surface. The carboxylic groups on oxidized carbon surface have cation exchange properties and oxidized carbons can be used as highly selective cationites.

The carboxylic groups on oxidized carbon surface have cation exchange properties and oxidized carbons can be used as highly selective cationites. Basic surface oxides are always present and carbons exhibit an anion exchange capacity too. The presence of surface oxides, together with chemical and radiation stability of oxidized carbons, provide their advantages over the synthetic resin cationites.

Table 2. BET surface area and pore volume of the samples determined by N_2 adsorption.

Sample	BET m^2/g	V_{tot} cm^3/g	V_{micro} cm^3/g	V_{meso} cm^3/g	V_{macro} cm^3/g	I_2 mg/g
POW-OC	500	0.586	0.263	0.120	0.203	490
POW-AC	513	0.600	0.270	0.140	0.190	600
FPOW-AC	1000	0.486	0.338	0.033	0.115	1200

CONCLUSION

Synthetic carbon adsorbents with different properties are obtained from polymer and biomass treatment products. They possess insignificant ash and sulfur content. The results from IR spectroscopy and Boehm titration show the presence of oxygen-containing surface groups. Porous structure and high content of surface groups of the activated carbon samples, produced from polyolefin wax characterize them as potentially effective adsorbents for different pollutants - heavy metals (oxidized sample), organics (physically activated sample), etc.

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ТЕРМООКИСЛИТЕЛНА КОНВЕРСИЯ НА ПОЛИОЛЕФИНОВ ВОСЪК ДО ВЪГЛЕРОДНИ АДСОРБЕНТИ

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(Резюме)

Въглеродни адсорбенти с различни свойства бяха получени на основата на фурфурол и смеси от фурфурол и полимерни отпадъци (полиолефинов восък) при различни условия на синтез и активиращи агенти. Получените въглени се характеризират с незначително пепелно съдържание. Бе установено, че обемът и разпределението на порите, както и химичният характер на повърхността, зависят от активиращия реагент и от температурата на термохимичната обработка. ИЧ спектрите и охарактеризирането на повърхностните групи по метода да Бьом показаха наличие на различни кислород-съдържащи групи с кисел и основен характер. Нашите изследвания показват, че на основата на полимерни отпадъци са получени различни активни въглени, които поради свойствата си са перспективни за приложение като ефективни адсорбенти на токсични метални и органични замърсители.