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## Synthesis of new carbon-nitrogen composites based on waste sweet drinks

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**Abstract:** The materials under investigation were new carbon-nitrogen composites obtained via pyrolysis and CO<sub>2</sub> activation of sweet drinks destined for utilization. Waste *Pepsi Cola*<sup>®</sup> has been examined as an alternative and renewable carbon source for composite materials. Nitrogen was introduced into the *Pepsi Cola*<sup>®</sup> solution via the addition of guanidine carbonate, before the pyrolysis process. The physicochemical properties of the materials studied were characterized by low-temperature nitrogen adsorption (using BET and BJH methods), elemental analysis, FTIR spectroscopy, scanning electron microscopy (SEM) as well as determination of pH<sub>pzc</sub> and the number of surface functional groups. Additionally, thermal properties of the samples were investigated by thermogravimetric analysis (TG) and differential thermogravimetry (DTG). The final products were new carbon-nitrogen composites characterized by a very high content of nitrogen (11.2 - 21.6 wt.%) as well as relatively low surface area and pore volume reaching 198 m<sup>2</sup>/g and 0.16 cm<sup>3</sup>/g, respectively. Results of FT-IR study and Boehm titration indicated that the composites surface has clearly basic character, which was confirmed by pH<sub>pzc</sub> values above 8.0.

**Keywords:** carbon-nitrogen composites, waste sweet drinks, activated carbon, physical activation, physico-chemical properties

### 1. Introduction

According to hitherto studies, also those conducted in our group, the activated carbons obtained from waste materials (e.g. nutshells, fruit stones, corn cobs, hay, sawdust and sludge from sewage treatment plants) can be used for effective removal of many organic and inorganic compounds both from gas and liquid phase (Wilson et al., 2006; Deng et al., 2009; Foo and Hameed, 2011; Nowicki et al., 2013). Moreover, the materials obtained by activation of these precursors are very often more effective adsorbents than the activated carbons synthesized from conventional precursors such as wood, peat or fossil coals of different metamorphism degree (Bazan-Wozniak et al., 2017; Kante et al., 2012; Nowicki et al., 2016). However, the use of such precursors is related to the problem of their varying quality (different content of carbon and other heteroatoms) because it depends on the time and place of harvesting and the problem of availability in a given area. Therefore, the use of post-agricultural precursors for production of carbon sorbents may lead to low reproducibility of the results of syntheses. The adsorbents obtained from e.g. hay growing in different regions of the country may show different sorption properties depending on the soil pH and the content of heteroatoms (nitrogen, sulfur, phosphorus) and other chemicals in the soil.

Growing demand for carbonaceous materials and increasingly stringent requirements regarding the natural environment protection stimulate the search for new precursors and new technologies of carbon materials production, including different chemical modifications, for example incorporation of nitrogen functional groups into carbonaceous structure via pre- or post-activation treatment (Gil et al., 2019; Samojeden and Grzybek, 2016; Kazmierczak-Razna et al., 2015; Nowicki, 2016). Nitrogen-enriched carbons are very popular in recent time, because of wide gamut of their practical application. Such

materials are used as adsorbents of toxic gases, dyes or heavy metal ions (Plaza et al., 2007; Nowicki et al., 2010; Goscianska et al., 2017; Zhu et al., 2010), as catalyst or catalyst support e.g. in oxidative adsorption of methyl mercaptan or NH<sub>3</sub>-SCR process (Bagreev et al., 2005; Klinik et al., 2011; Grzybek et al., 2008), for hydrogen storage (Giraudet and Zhu, 2011) as well as electrical energy storage in electrochemical capacitors (Kazmierczak-Razna et al. 2019; Jurewicz et al., 2008).

The necessity of the natural environment protection implies development of the so-called "green technologies", restriction of the use of nonrenewable resources and finding the sources of carbon containing waste in controlled and stable amounts, produced in large amounts and easily available. Such resources for production of activated carbon can be e.g. sweet drinks that are no longer drinkable and are destined for utilization. For example, *Pepsi Cola*<sup>®</sup> has high content of carbon as sugars, provides *in-situ* doping of O, N and S and has constant composition, as opposed to other conventional biomass materials, making it an attractive and cheap alternative for synthesis of new carbon materials. The production of only *Pepsi Cola*<sup>®</sup> reaches about 1 mld 1-litre bottles a day (in USA in 2011 as much as 1334,9 mln gallons), and the composition of the liquid is the same. This type drinks contain about 11 g of sugar (glucose and fructose) in 100 cm<sup>3</sup>, which means that they are rich source of carbon. Moreover, they contain caramel dye E150d (often containing 4-methylimidazole of the formula C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>), orthophosphoric acid, natural aromas (essential oils, extracts from fruit and spices) and caffeine (C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>) in the amount of about 0.01 g/100 cm<sup>3</sup>, which makes them attractive because nitrogen, sulfur and phosphorus are valuable admixtures in the structure of the carbonaceous materials (<https://www.pepsico.com/docs/album/annual-reports/pepsico-inc-2016-annual-report.pdf>, 2016).

In the present work, we report for the first time on the method for preparing carbon-nitrogen composites by using waste *Pepsi Cola*<sup>®</sup> from nearby restaurants and shops as carbon precursor and guanidine carbonate as nitrogenating agent. Moreover, FT-IR spectroscopy, low-temperature nitrogen sorption, elemental analysis, Boehm method were used to determine the physicochemical properties of the carbon material obtained and to check the influence of nitrogen doping on its textural, acid-base and thermal properties.

## 2. Materials and methods

### 2.1. Samples preparation

Waste sweet drink *Pepsi Cola*<sup>®</sup> (P), containing about 11 g of sugar (in glucose and fructose form) in 100 cm<sup>3</sup>, was used as the starting material. At the beginning the starting *Pepsi Cola*<sup>®</sup> was divided into two parts. One of them was subjected to impregnation with nitrogenating agent – guanidine carbonate (impregnation weight ratio 1:1) and dried at 105 °C to a constant mass. The remaining part of starting material was dried in analogous conditions without impregnation. After drying, both samples were subjected to pyrolysis in a horizontal furnace under a stream of argon blown at the rate of 0.170 dm<sup>3</sup>/min. The samples were heated (10 °C/min) from room temperature to the final pyrolysis temperature of 500 °C (PP and N-PP samples, respectively). In the final pyrolysis temperature, the samples were kept for 60 min and then cooled down. The products of pyrolysis were next subjected to physical activation with CO<sub>2</sub> (PPA and N-PPA samples, respectively). Physical activation was employed in order to keep as much as possible of the nitrogen functional groups, introduced earlier into carbon structure. This process was carried out at temperature of 800 °C, under a stream of carbon dioxide with the flow rate of 0.250 dm<sup>3</sup>/min, for 30 min.

### 2.2. Characterisation of materials obtained

Elemental analysis of samples was performed by using an elemental analyzer CHNS Vario EL III provided by Elementar Analysensysteme GmbH, Germany. The content of ash was determined according to the Data National Standards ISO 1171:2002.

Characterization of the pore structure of activated carbons was determined by nitrogen adsorption – desorption at -196 °C by Autosorb iQ surface area analyzer (Quantachrome Instruments USA). On the grounds of results of these measurements the BET surface area, total pore volume and average pore diameter were determined. The total pore volume ( $V_t$ ) was calculated at a relative pressure of approximately  $p/p_0 = 0.99$  and at this relative pressure all pores were completely filled with nitrogen.

The average pore diameter ( $D$ ) was determined on the basis of the surface area ( $S$ ) and the total pore volume ( $V_t$ ) according to the formula  $D = 4V_t/S$ . Moreover, micropore volume ( $V_{mic}$ ) and micropore area ( $S_{mic}$ ) were calculated using the t-plot method.

The analysis of surface functional groups content was performed based on the Boehm method (Boehm, 1994) Briefly: the carbon samples (0.25 g) were added to 25 cm<sup>3</sup> of NaOH or HCl solutions (in the concentration of 0.1 mol/dm<sup>3</sup>) and shaken for 24 h. Next, 10 cm<sup>3</sup> of each filtrate was pipetted and titrated with HCl or NaOH (concentration 0.1 mol/dm<sup>3</sup>), respectively. The point of zero charge  $pH_{pzc}$  was determined by means of a pH meter manufactured by Metrohm Ion Analysis (Switzerland) equipped with Unitrode Pt1000 (combined glass pH electrode with temperature sensor), calibrated with standards solutions of pH 3, 7 and 10. For this purpose 0.01 mol/dm<sup>3</sup> NaCl solution pH was adjusted between 2 and 12 by adding 0.1 mol/dm<sup>3</sup> NaOH and 0.1 mol/dm<sup>3</sup> HCl. A portion of 0.2 g of the sample was added to 50 cm<sup>3</sup> of the solution. This mixture was agitated properly and the final pH of the solution was obtained after 24 h of shaking.

The Fourier transform infrared spectroscopy (FTIR) was used to identify the functional groups present on the surface of composites. The measurements were conducted by means of 6700 type A FTIR spectrometer (Jasco, USA). The spectra were recorded in the wavenumber range of 400-4000 cm<sup>-1</sup>.

Morphology of the samples obtained was analyzed on the basis of a scanning electron microscope (Hitachi S-3400N) images recorded using acceleration voltage of electron beam adjusted to 15 keV.

Thermogravimetric analysis of the all samples was performed on a SETSYS 12 made by Setaram. The samples (10 mg, particle size below 0.06 mm) were heated at the rate 5 °C/min, in helium atmosphere. Analysis lasted 100 min and the temperature during the decomposition varied from 20 to 1000 °C.

### 3. Results and discussion

#### 3.1. Elemental composition of the samples

Table 1 presents the results of elemental analysis of the char (PP) and activated carbon (PPA) obtained from *Pepsi Cola*<sup>®</sup> destined for utilization because of long overdue expiry date. Upon water evaporation the chemical and physical changes in the initial material were noted like increased density, change in color from light brown to black, the appearance of a characteristic smell of burnt caramel and intensive foaming. These changes are related to caramelization of carbohydrates present in the precursor structure. The first to change the color is fructose as its caramelization starts already at about 110 °C. Then the process of condensation takes place in which particular sugars lose water molecules and react with each other to form e.g. fructose and glucose anhydrides. Further thermal treatment leads to isomerization of aldoses to ketoses and progressing dehydration. Finally, a number of reactions take place including the reactions of decomposition evidenced by smell (excretion of odor compounds) and polymerization (changes in color) (Zenkevich et al., 2002). As a result of thermal treatment of *Pepsi Cola*<sup>®</sup> in the atmosphere of neutral gas, a char PP was obtained. Its degree of coalification was close to 80.3 wt.% and it contained 3.7 wt.% of hydrogen and 15.4 wt.% of oxygen, which suggests the presence of surface oxygen groups of acidic character.

Table 1. Elemental analysis of the materials obtained; the yield of pyrolysis and activation process (wt.%)

Sample	Ash	C <sup>daf</sup> *	H <sup>daf</sup>	N <sup>daf</sup>	S <sup>daf</sup>	O <sup>diff**</sup>	Yield
PP	0.0	80.3	3.7	0.5	0.1	15.4	29.6
PPA	2.3	93.1	1.5	1.6	0.2	3.6	75.2
N-PP	0.0	62.7	3.6	21.6	0.2	11.9	21.8
N-PPA	4.1	78.0	2.0	11.2	0.4	8.3	59.0

\* dry-ash-free basis; \*\* determined by difference

The product of activation (PPA) shows a considerably higher content of carbon, nitrogen and sulfur than char PP, but also a much lower content of hydrogen and oxygen. The increase in the content of C<sup>daf</sup> is a result of changes in the structure of organic carbon upon activation, a decrease in the content of heteroatoms and a decrease in the aliphatic character at a simultaneous increase in the content of thermally stable aromatic structures. The increase in the content of N<sup>daf</sup> suggests that this element occurs

in the precursor in the form of thermally stable heterocyclic connections and because of the loss of oxygen by the carbon substance its content significantly increases. As mentioned above, the process of activation also affects the content of hydrogen. The decrease in  $H^{daf}$  content is related to the effect of high temperature breaking the less stable chemical bonds in the product of activation and progressing aromatization of the carbon structure leading to formation of numerous side products of activation, rich in hydrogen, which leads to elimination of this element. The activated carbon obtained also shows much lower content of oxygen than PP. The considerable loss of oxygen upon activation is caused by oxidation of the char leading to formation of rich in oxygen gas side products.

Table 1 includes also the content of carbon, hydrogen, nitrogen, sulfur and oxygen in carbon-nitrogen composites obtained from *Pepsi Cola*<sup>®</sup>. N-PP composite obtained from the sweet drinks and guanidine carbonate upon thermal treatment at 500 °C for 60 min, in nitrogen atmosphere, is characterized by very high content of nitrogen (21.6 wt.%). This content is much higher than in carbon-nitrogen composites obtained from activated carbon and melamine at the 1:1 ratio that contains only 15.4 wt. % of nitrogen (Feng et al., 2015). Such a high content of nitrogen could not have been obtained by direct activation of hay impregnated with urea, with the use of microwave heating, that contained  $N^{daf} = 12.8$  wt.% (Kazmierczak-Razna et al., 2015). Only amoxidation (simultaneous oxidation and nitrogenation) of brown coal gave a substance with a comparable content of nitrogen of  $N^{daf} = 23.4$  wt.% (Nowicki et al., 2008).

The activation of the composite with carbon(IV) oxide at 800 °C led to destruction of a significant number of the earlier introduced nitrogen groups and/or their transformation to more thermally and chemically stable species incorporated in deeper layers of the carbon structure. The process of activation also leads to significant changes in the content of the other elemental components of the composite, carbon, hydrogen and oxygen. The content of elemental carbon and sulfur increase, while the contents of elemental hydrogen and oxygen decrease because of further aromatization of the carbon structure.

### 3.2. Porous structure parameters

All the materials obtained were characterized by determination of the surface area by the BET method, total pore volume and mean pore diameter, while the area and volume of micropores were determined by the t-plot method. As follows from the results presented in Table 2, the temperature and time of pyrolysis and activation did not lead to proper ordering of the carbon substance and development of a system of pores. Only sample N-PPA was characterized by moderately developed surface area of 198 m<sup>2</sup>/g and pore volume of 0.157 cm<sup>3</sup>/g, of which 62% is the volume of micropores. The mean pore diameter in this composite is 3.184 nm, which evidences the presence of a considerable contribution of mesopores, confirmed by the pore size distribution presented in Fig. 1. The low surface area of the obtained composites suggests that they may not be very effective as adsorbents. However, they can be excellent supports for catalysts, e.g. for the NH<sub>3</sub>-SCR process. Particularly preferably in this regard is the N-PPA sample, characterized at the same time with a high nitrogen content.

The most probable reason for development of the porous structure in the composite modified with nitrogen and subjected to pyrolysis and activation is the enhanced reactivity of the modified precursor resulting from the presence of a significant number of nitrogen and oxygen groups introduced upon impregnation, that can contribute to the carbon activation. Probably in the process of pyrolysis of the sample modified at the stage of precursor, a significant part of the nitrogen groups introduced upon impregnation undergo decomposition, while the rest is transformed to more thermally stable species and is incorporated into deeper layers of the carbon structure. Upon activation these groups react with the activating agent and undergo decomposition (manifested as a drastic decrease in the content of nitrogen), thus facilitating the access of the activating agent to deeper layers of the char and leading to stronger development of the porous structure (Nowicki et al., 2008).

From the aspect of realization of the aims of this study it was also important to analyze the morphology of pure char, activated carbon as well as the carbon-nitrogen composites. The samples were subjected to scanning electron microscopy (SEM) study. Figure 2a and 2b present the images of fragments of surfaces of samples PP and PPA obtained by pyrolysis and further activation of unmodified precursor. The images show the lamellar structure of grains of irregular shapes but it is hard to notice any pores. The SEM images of carbon-nitrogen composites (Fig. 2c and d) show grains of

spherical and lamellar shapes. Figure 2d illustrates also that activation of N-PP composite leads to generation of the system of pores.

Table 2. Textural parameters of the chars and activated carbons

Sample	Surface area (m <sup>2</sup> /g)		Pore volume (cm <sup>3</sup> /g)		Micropore contribution	Average pore diameter (nm)
	Total	Micropore	Total	Micropore		
PP	8	~1	0.023	0.001	0.04	13.462
PPA	64	46	0.070	0.027	0.38	4.235
N-PP	16	~6	0.030	0.005	0.16	7.457
N-PPA	198	163	0.157	0.098	0.62	3.184

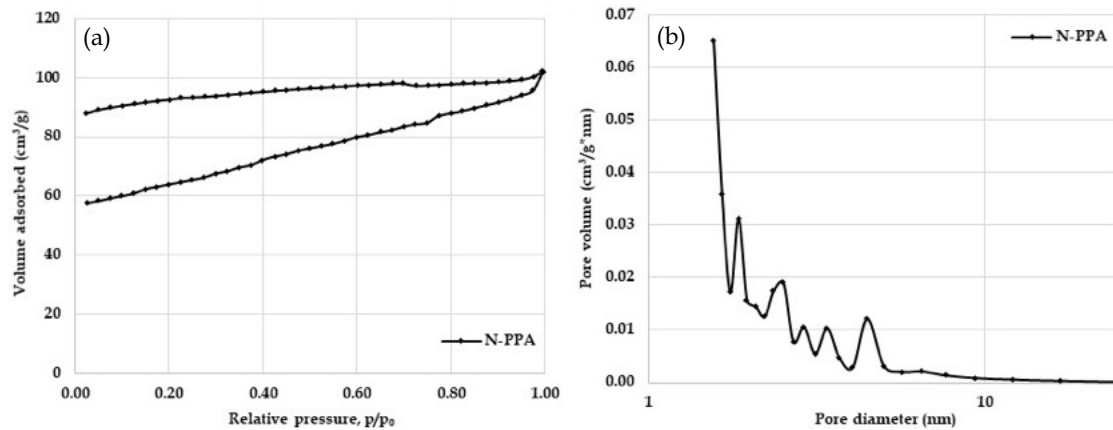


Fig. 1. Nitrogen adsorption/desorption isotherm (a) and pore size distribution (b) for N-PPA sample

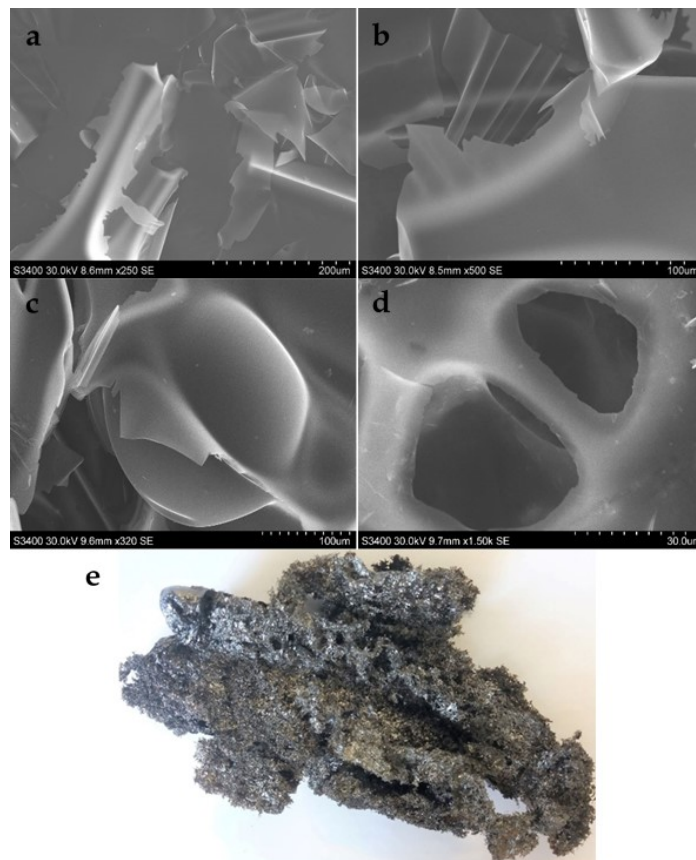


Fig. 2. SEM micrographs of the samples: PP (a), PPA (b), N-PP (c), N-PPA (d) and photograph of N-PPA composite (e)

### 3.3. Acid–base properties of the samples

In order to characterize the chemical properties of the surface of all samples obtained, the content of the content of surface functional groups of acidic and basic type as well as  $\text{pH}_{\text{PZC}}$  were measured. According to the data collected in Table 3, the product of pyrolysis of the precursor (sample PP) has basic and acidic surface groups, but the acidic ones dominate. The char exposure to carbon(IV) oxide leads to total destruction of groups of acidic character, but at the same time to generation of new groups of basic character. Consequently, the value of  $\text{pH}_{\text{PZC}}$  increases from 7.68 for PP to 7.98 for PPA. In each N-doped composite obtained the basic groups are dominant and the  $\text{pH}_{\text{PZC}}$  value of the composites is much higher than 8. Sample N-PPA has almost twice greater content of acidic groups than the char modified with nitrogen N-PP. The content of basic groups is almost the same in these two samples. A small decrease in  $\text{pH}_{\text{PZC}}$ , as a result of activation, can suggest that these groups are of weakly acidic character, for example phenolic or carbonyl groups.

Table 3. Acid-base properties of the samples obtained

Sample	$\text{pH}_{\text{PZC}}$	Acidic groups (mmol/g)	Basic groups (mmol/g)	Total content (mmol/g)
PP	7.68	0.47	0.08	0.53
PPA	7.98	0.00	0.35	0.35
N-PP	8.50	0.38	1.25	1.63
N-PPA	8.34	0.80	1.23	2.03

### 3.4. Surface chemistry of samples

Figure 3a shows the FTIR spectra of PP and PPA samples. In the spectrum of sample PP, the main peaks are attributed to caffeine or products of its transformation, as a result of the heat treatment (El-Abassy et al., 2015). The broad peak at  $3500\text{--}3000\text{ cm}^{-1}$  and the narrow peak at  $3600\text{ cm}^{-1}$  correspond to O–H groups. The small peak at  $2900\text{ cm}^{-1}$  corresponds to the stretching of C–H group. The peak at  $2400\text{--}2300\text{ cm}^{-1}$  can be attributed to  $\text{CO}_2$ . The peaks at  $1700\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  represent N–H groups and C=O groups. The presence of peaks in the range of  $1430\text{--}1300\text{ cm}^{-1}$  can be attributed to the stretching vibration mode of C–N, imidazole ring and the deformation of C–H, respectively. Peaks at  $1400$ ,  $1100\text{ cm}^{-1}$  and  $1030\text{ cm}^{-1}$  can be assigned to the symmetric stretching vibration mode of C–N, the deformation mode of C–C and asymmetric stretching of N– $\text{CH}_3$ , respectively. The deformation vibration modes for all of CH–N, N–C–H, O=C–C and C–N–C are observed at  $1250$ ,  $800$ ,  $750$  and  $480\text{ cm}^{-1}$ , respectively.

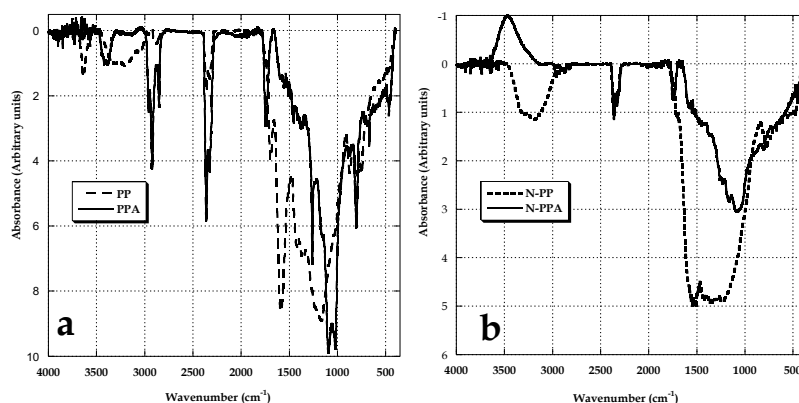


Fig. 3. FTIR spectra of the samples obtained from Pepsi Cola® (a) and N-doped Pepsi Cola® (b)

The activation by  $\text{CO}_2$  and heating at  $800\text{ }^\circ\text{C}$  significantly changes the chemical structure of PP char. Some of the bands visible for PP disappear in the FTIR spectrum of PPA sample, while some other peaks become more intense. The peak observed at  $3400\text{ cm}^{-1}$  can be attributed to the typical stretching vibrations of O–H groups, including hydrogen interactions. The bands at  $3000\text{--}2700\text{ cm}^{-1}$  are due to

the C=O and C–H stretching vibrations of aliphatic compounds. The peak at  $1750\text{ cm}^{-1}$  is probably attributed to the C=O stretching vibration of non-aromatic carboxyl groups. The bands close to  $1100\text{ cm}^{-1}$ , indicate the presence of a C–O single bond, such as that in alcohols, phenols, acids, ethers or esters. The bands around  $800\text{--}500\text{ cm}^{-1}$  can be attributed to C–H, C=N and  $\text{CH}=\text{CH}_2$  stretching vibrations in aromatic structures (Zawadzki and Wiśniewski, 2003).

Somewhat different FTIR spectra were recorded for the carbon-nitrogen composites (Fig. 3b). The bands at  $3400\text{--}3000\text{ cm}^{-1}$ , observed in the N-PP spectrum, and near  $3500\text{ cm}^{-1}$  in the N-PPA spectrum can be attributed to the typical stretching vibrations of O–H groups. The peak of medium height at  $2400\text{--}2300\text{ cm}^{-1}$  observed in the N-PP and N-PPA spectra is related to  $\text{CO}_2$ . The band at  $1700\text{ cm}^{-1}$  observed in the N-PPA spectrum and near  $1560\text{ cm}^{-1}$  in the N-PP spectrum is related to C=O. The band at  $1600\text{--}1500\text{ cm}^{-1}$ , can be ascribed to aromatic skeletal vibrations, as well as to structures containing  $\text{--C=N--}$  bonds, e.g. pyridinic or lactams structures (Yu et al., 2014). The peak near  $1400\text{ cm}^{-1}$  in the N-PP spectrum can be associated with a  $\text{--COO--}$  asymmetric vibration of carboxylic groups. The spectrum of N-PPA exhibits also absorption bands close to  $1100\text{ cm}^{-1}$ , indicating the presence of a C–O single bond. A small band observed for the carbon-nitrogen composites at a wavelength of about  $800\text{ cm}^{-1}$ , can be assigned to cyclic structures containing conjugated C=C and C=N bonds. This band is more intense in the spectrum of N-PP sample, probably due to the lower nitrogen content in the activation product.

### 3.5. Thermal analysis

In order to determine the thermal stability and to confirm the presence of functional groups on the samples surface, they were subjected to thermogravimetric analysis. The thermograms are shown in Fig. 4. The first mass loss, visible in TG curves recorded for all samples (Fig. 4a), at about  $100\text{ }^\circ\text{C}$ , corresponds to desorption of physisorbed water. The thermograms imply that the char PP and the activated carbon PPA obtained from unmodified *Pepsi Cola*<sup>®</sup> show only about 5% mass loss up to about  $500\text{ }^\circ\text{C}$ , which indicates their much higher thermal stability than that of the analogous samples obtained from the precursor modified with nitrogen, N-PP and N-PPA. The thermal stability of sample PP drastically decreases above  $500\text{ }^\circ\text{C}$ , which is related to the process of secondary degassing as a consequence of decomposition of oxygen and nitrogen functional groups in the sample structure. Much more thermally stable was sample PPA. For the latter sample a significant mass loss was observed at temperatures higher than  $700\text{ }^\circ\text{C}$ , which can be assigned to slow degradation of carbon matrix resistant to thermal conditions applied during the activation stage. The TG curves of the two samples of carbon-nitrogen composites are similar, but the mass loss in the corresponding temperature range is much greater. It is particularly pronounced for sample N-PP in the range  $500\text{--}800\text{ }^\circ\text{C}$ . This drastic mass loss related to the process of secondary degassing is a consequence of a high content of nitrogen in its structure 21.6 wt.% (Table 1). To some degree it is confirmed by the fact that for sample N-PPA, containing only 11.2 wt.% of nitrogen, the mass loss observed in this temperature range is by about 10% smaller. Intense mass loss observed for both samples in the range  $900\text{--}1000\text{ }^\circ\text{C}$  is probably caused by extensive gasification of carbon matrix.

The DTG curve recorded for sample PP shows three minima, the first of them ( $\text{DTG}_{\text{min}} \sim 50\text{ }^\circ\text{C}$ ) corresponds to elimination of adsorbed water. The second peak, appearing above  $200\text{ }^\circ\text{C}$  corresponds to decomposition of the least thermally stable oxygen and nitrogen functional groups present in the structure of the char. The third peak above  $550\text{ }^\circ\text{C}$  can be with a high probability assigned to decomposition of the remaining oxygen and nitrogen functional groups (e.g. phenol, ether, carbonate, carbonyl, pyrrole and pyridine ones) and gasification of the least thermally stable fragments of the activated carbon structure. The DTG curve for sample N-PP, obtained from nitrogen-enriched precursor, also shows three peaks but their intensities and temperatures at which they appear are a bit different. The intensity of the peak ( $\text{DTG}_{\text{min}} \sim 50\text{ }^\circ\text{C}$ ) corresponding to elimination of physisorbed water is about three times higher than in the DTG curve for sample PP, which suggests that incorporation of significant amount of nitrogen and/or oxygen functional groups causes a considerable increase in the hydrophilic properties of the samples' surfaces. The second peak, in the range of  $200\text{--}300\text{ }^\circ\text{C}$ , probably corresponds to decomposition of nitrogen groups showing low thermal stability and introduced in the sample structure prior to pyrolysis, for example amines, imines and lactams. A broad band in the range

of 400-800 °C can be with a high probability assigned to the loss of volatile matter and decomposition of nitrogen groups in which nitrogen is built into the aromatic ring, so pyridine, pyrrole or pyridine N-oxide (Kazmierczak-Razna et al., 2015). Results of the thermogravimetric study and elemental analysis (Table 1) confirm that a significant amount of nitrogen introduced into the structure of the precursor in the reaction with guanidine carbonate, show low thermal stability.

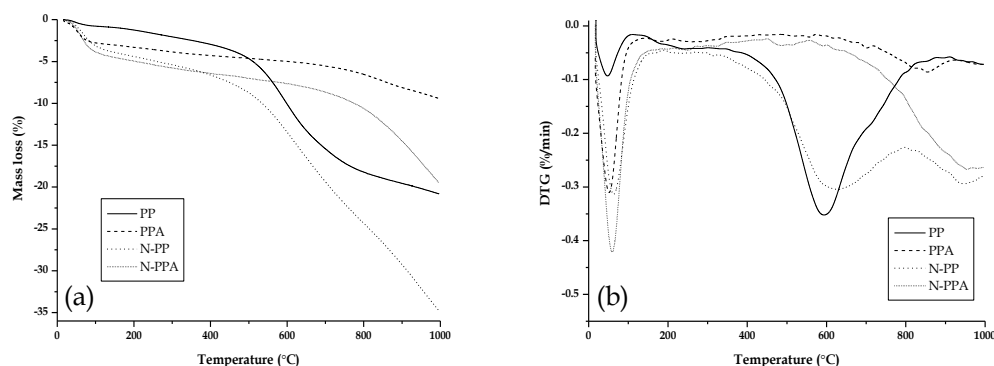


Fig. 4. TG (a) and DTG (b) curves of the samples obtained

As a result of annealing of PP and N-PP chars in carbon dioxide atmosphere at 800 °C, the thermal stability of the samples considerably increases. It is clearly evidenced by the lower mass loss as well as by the lower intensity of particular minima observed on DTG curves for PPA and N-PPA and the shift of these minima to higher temperatures. The DTG curves show two main bands, one corresponding to elimination of physisorbed water ( $DTG_{min} \sim 50-60$  °C), while the second one to the decomposition of more thermally stable nitrogen groups and oxygen functional groups generated upon activation on the activated carbon surface (a broad band above 800 °C). The DTG curves of activated carbons (similarly as those of chars) show a small minimum in the range of 200-400 °C, most probably attributable to decomposition of thermally labile oxygen functional groups introduced in the structure during the process of activation, e.g. carboxyl and lactone groups (Nowicki, 2016).

#### 4. Conclusions

The above presented and discussed results show that waste *Pepsi Cola*<sup>®</sup> and guanidine carbonate can be successfully used to prepare carbon-nitrogen composites with high content of nitrogen. Thermogravimetric results have shown that the majority of nitrogen incorporated into the carbon structure occurs in the form of functional groups of low thermal stability that undergo decomposition upon pyrolysis and activation. That is why future attempts should be made to introduce nitrogen at the stage of char, which should increase the content of nitrogen remaining in the structure of the final product. Unfortunately, the majority of samples obtained, except sample N-PPA, show rather poor textural parameters. Improvement of textural parameters can be achieved by a change in the temperature-time regime of particular technological processes and the use of more reactive activating agents, e.g. carbonates or sodium or potassium hydroxides or phosphoric acid. The improvement of the textural properties of the materials can significantly extend the spectrum of their potential use.

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