Textural development of sugar beet bagasse activated with $ZnCl_2$

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Abstract

In this study, activated carbons were prepared from sugar beet bagasse, which is side product and waste in sugar plants, by chemical activation with $ZnCl_2$. Influence of activation temperature was investigated on to pore structure. $ZnCl_2$/sugar beet bagasse ratio (impregnation ratio) was selected as 1:1. The impregnated sample was raised to the activation temperature under N_2 (100 ml/min) atmosphere with 10 °C/min heating rate and hold at this temperature for 1 h. The activation temperature was varied over the temperature range of 400–900 °C. BET surface area values were determined in the range of 832–1697 m^2/g. Under the experimental conditions, 500 °C was found to be the optimal condition for producing high surface area carbons with $ZnCl_2$ activation. Sugar beet bagasse was suitable for preparation of activated carbon with essentially microporous structure. Activated carbon ash content was found in the range of 1.2–2.7 (%w/w d.b.). Activated carbon samples and raw material were characterized by XRD, FT-IR, DTA and TGA.
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1. Introduction

Activated carbon produced from environmental waste with high carbon content is the most important material to clean environmental pollution (gases and liquid impurities). Environmental wastes are very important starting material for preparing activated carbon. Various polymeric wastes, based on petroleum, agriculture by-product (ligno-cellulosic) and coals, are commonly used as a starting material for preparing activated carbon [1].

The qualities and characteristics of activated carbon depend on the physical and chemical properties of the starting materials and activation methods. Activated carbon is classified to one of three types; such as powder activated carbon (PAC), granular activated carbon (GAC) and fibrous activated carbon (ACFs) [2,3].

There are basically two methods for preparing activated carbon: physical and chemical activation. Physical activation (called thermal) consists of two steps: activation of starting material and activation of the char by using carbon dioxide or steam.

In chemical activation, the starting materials are impregnated with an activating agent ($ZnCl_2$, NaCl, Na_2CO_3, K_2CO_3, KOH, NaOH, Al_2O_3, H_3PO_4, H_2SO_4, NH_4Cl, etc.) [4–12]. Impregnated material is heated in an inert atmosphere (N_2, Ar and CO_2 atmosphere). Type of activating agent, impregnation ratio, activation temperature and activation time are related with different physical and chemical characteristic of the products. KOH and $ZnCl_2$ is the widely used chemical agent to obtain high surface area in the preparation activated carbon [13–18]. These two chemicals have been chosen for two reasons. The first reason is being KOH the most effective alkali salt in the production of activated carbon and the second reason is to study the influence of different chemical – strong base (KOH) and Lewis acid ($ZnCl_2$) – on the structure of the activated carbon products. In addition, KOH and $ZnCl_2$ have increasingly been used as activation reagents, since they result in high surface areas and high yield. Chemical activation process normally takes place at a temperature lower than that used in physical activation process, therefore it improve the pore development in the carbon structure.

In this study, the effect of activation temperature on the AC samples prepared from sugar beet bagasse that is an industrial waste was investigated by chemical activation with $ZnCl_2$.

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Table 1
Elemental analysis, ash content and activation yield of the raw material and the activated carbons from sugar beet bagasse

Samples	C (wt.% d.b.)	H (wt.% d.b.)	N (wt.% d.b.)	S (wt.% d.b.)	O (diff) (wt.% d.b.)	Ash (%)	Activation yield (w/w%)
Raw material	46.5	7.00	2.18	0.19	44.1	3.95	–
KKZn4	70.0	2.07	1.36	0.05	26.5	2.72	34
KKZn5	79.4	2.43	1.24	0.14	16.8	1.37	37
KKZn6	81.5	2.09	1.24	0.11	15.1	1.21	35
KKZn7	81.0	1.64	1.36	0.09	15.9	1.83	36
KKZn8	81.2	1.51	1.11	0.10	16.1	1.81	33
KKZn9	80.1	1.00	0.84	0.09	18.0	2.13	32

d.b., dry bases.

2. Experimental

2.1. Activated carbon preparation

Brought in 20 kg containers, sugar beet bagasse supplied by Malatya sugar plant (Turkey, 68,400 tonnes/year) were dried under laboratory conditions and then dried again at 100 °C (Model FN 400, Nüve) until it reaches a constant weight. Starting material were stored in plastic bottle after grounding. All experiments carried out with this sample. The characteristic of sugar beet bagasse are listed in Table 1.

In the first step of activation, the starting material was mixed with $ZnCl_2$ at the $ZnCl_2$/starting material weight ratio of 1:1 and the mixture was kneaded with adding distilled water. The mixture was then dried at 110 °C to prepare the impregnated sample.

In the second step, the impregnated sample was placed on a quartz dish, which was then inserted in a quartz tube (i.d. = 60 mm). The impregnated sample was heated up to activation temperature under N_2 flow (100 ml min^{-1}) at the rate of 10 °C min^{-1} and hold at the activation temperature for 1 h. The activation temperature was varied over the temperature range of 400–900 °C (samples is coded KKZn4, KKZn5, KKZn6, KKZn7, KKZn8, KKZn9). After activation, the sample was cooled down under N_2 flow and 0.5N HCl was added on to activated sample. Activated sample was washed sequentially several times with hot distilled water to remove residual chemical until it did not give Cl reaction with $AgNO_3$. The washed sample was dried at 110 °C to prepare activated carbon.

2.2. Characterization of pore structure

A Tri Star 3000 (Micromeritics. USA) was used to measure nitrogen adsorption isotherm at 77 K in the range of relative pressure 10^{-6} to 1. Before measurement all sample were out gassed at 300 °C for 2 h. The surface areas were calculated by the BET (Brunauer–Emmett–Teller) method assuming that the surface area occupied by per physisorbed nitrogen molecule was 0.162 mn^2. The total pore volumes were estimated to be the liquid volume of N_2 at relative pressure (P/P_o) of 0.9814. The t-plot method was applied to calculate the micropore volume and mesopore surface area, and mesopore volume was determined by subtracting the micropore volume from total pore volume. The average pore radius were estimated from BET surface area and total pore volume assuming an open-ended cylindrical pore model without pore networks and from BJH (Barret–Joymer–Halenda) method [19].

2.3. Characterization of AC samples

Thermal analysis was carried out in thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) apparatus (Shimadzu DTA 50 and TGA 60, Japan). Samples were loaded in to a platinum pan and heated to 1000 °C with a controlled heating rate of 10 °C min^{-1} under N_2 atmosphere.

Each sample was mixed with potassium bromide in 0.1 wt.% ratio and used for FT-IR analysis. Samples were dried under vacuum at 110 °C prior to mixing with KBr powder. The mixture was finally ground and then vacuum dried at approximately 110 °C. XRD patterns were obtained by a Rigaku Giegerflex D-Max/B powder diffractometer with Cu K$_\alpha$ radiation. Elemental analysis of the samples was performed in Leco CHNS 932 (USA) analyzer.

3. Results and discussion

3.1. Ultimate analyses

The results of ultimate and proximate analyses of the sugar beet bagasse activated carbons prepared at 400–900 °C for 60 min are shown in Table 1.

It can be seen that as a starting material for activated carbons, the sugar beet bagasse has a relatively high carbon content (46.5%) and low ash content (3.95%), which are desirable for good adsorbent. After activation, ash content had decreased to as low as 1.21% while the carbon content increased to as high as 81.5% with activation at either 400 or 600 °C. They have predominantly carbon content. However, when the activation temperature was increased to 700 or 900 °C, the carbon content commenced to decrease due to conversion of carbon into gaseous products (carbon monoxide). As the activation temperature increased from 400 to 900 °C, the hydrogen (H) and oxygen (O) content decreased progressively due to the continual release of volatile matters. The carbon (C) content of activated carbon, which was prepared at 400–900 °C, could reach as high as 81%C.
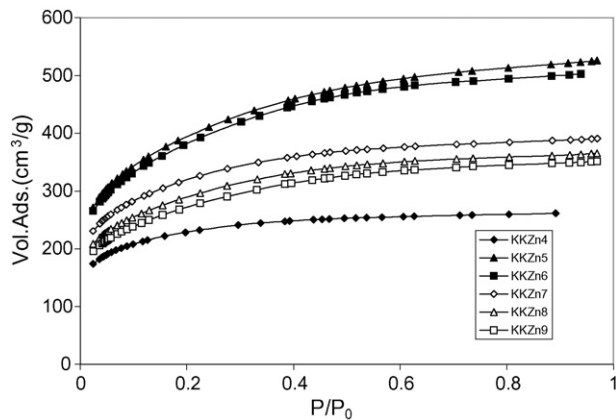
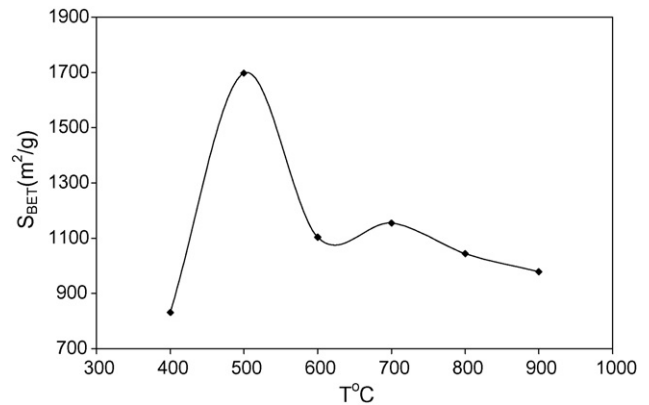Fig. 1. Adsorption isotherms of the activated carbons prepare from sugar beet bagasse under various temperature.

Fig. 2. Influences of activation temperature on the surface area of activated carbon.

3.2. Adsorption isotherms, surface area and micropore surface area

Nitrogen adsorption is a standard procedure for the determination of porosity of carbonaceous adsorbents. The adsorption isotherm is the information source about the porous structure of the adsorbent, heat of adsorption, characteristics of physics and chemistry and so on. For pore size definition, IUPAC standard was used and pore structure was defined as follows: micropore = width less than 2 nm; mesopore = width from 2 to 50 nm; macropore = width greater than 50 nm. Micropores can be divided into two groups; ultramicropores (width less than 0.5 nm) and supermicropores (width from 1 to 2 nm). Nitrogen adsorption isotherm of KKZn series shows a Type II isotherm in BDDT classification [20], as illustrated in Fig. 1. Type II isotherms can be obtained from carbons with mixed micro- and mesoporosity. The porous structure parameters derived from nitrogen adsorption isotherms analysis are listed in Table 2.

The adsorptive capacity of activated carbon is related to its specific surface area, pore volume and pore size distribution. Generally, as the surface area of the activated carbon increases, its adsorptive capacity will also increase. These surface areas are generated gradually during the activation processes. Activation temperature is the most important parameter for the processes. The effects of activation temperature on the BET surface area of the activated carbons are shown in Fig. 2. Increasing the activation temperature from 400 °C up to optimum value causes

an increase on the BET surface area and the surface area starts to decrease after this temperature. A sharp decline in the BET surface area was observed when the activation temperature was increased from 500 to 900 °C. This phenomenon was largely due to the excessive burn-off of carbon constituents at these high temperatures. The adsorptive capacity has the lowest value for the carbon prepared at 400 °C but it reaches maximum at 500 °C. The maximum surface area (1697 m^2/g) was obtained at the activation temperature of 500 °C. Increase in activation temperature can attribute to the increase in porosity by increasing the release of volatile matter. Activation temperature affects not only the BET surface area but also the micropore surface areas of activated carbon. Fig. 3 shows the micropore surface areas of activated carbons treated at different activation temperature. The highest micropore area was determined with the activation temperature at 700 °C. Activated carbon was predominantly microporous at 700 °C. Fig. 4 shows the micropore, mesopore and total volumes of activated carbons as a function of activation temperatures.

In addition, Fig. 5 shows that the effect of activation temperature on the BJH adsorption average pore diameter and adsorption average pore diameter (4V/A by BET). BJH adsorption average pore diameter and adsorption average pore diameter increases at activation temperature of 400–500 °C. Trend changes at 700 °C. This suggests that the carbon-ZnCl$_2$ reaction may occur at 700 °C for sugar beet bagasse.

Table 2
Effects of the activation temperature on the surface properties of the activated carbon

AC samples	S_{BET} (m^2/g)	S_{Mic} (m^2/g)	S_{Ext} (m^2/g)	S_{BJH} (m^2/g)	V_{Mic} (cm^3/g)	V_{BJH} (cm^3/g)	V_{Meso} (cm^3/g)	dp[a] (nm)	dp[b] (nm)
KKZn4	832	324	445	421	0.15	0.25	0.10	2.04	2.37
KKZn5	1697	318	1044	759	0.13	0.51	0.38	2.31	2.67
KKZn6	1104	284	1016	751	0.12	0.50	0.38	2.30	2.65
KKZn7	1155	404	785	665	0.17	0.42	0.25	2.13	2.52
KKZn8	1044	301	719	618	0.13	0.40	0.27	2.19	2.56
KKZn9	979	307	689	642	0.13	0.42	0.29	2.26	2.64

S_{BJH}, BJH cumulative surface area; V_{BJH}, BJH cumulative pore volume.
[a] dp, Adsorption average pore diameter by BET.
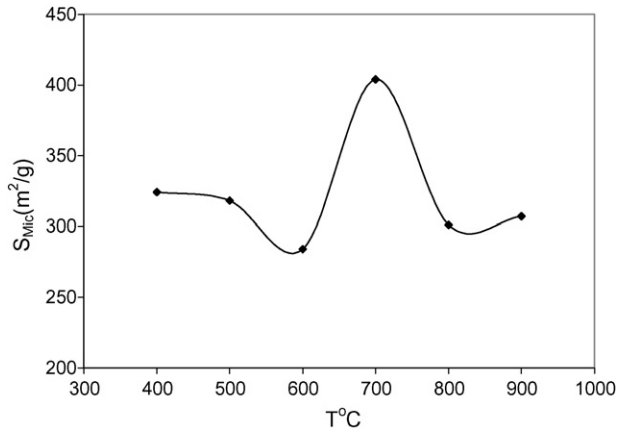[b] dp, Adsorption average pore diameter by BJH.

Fig. 3. Influences of activation temperature on the micro pore surface area of activated carbon.
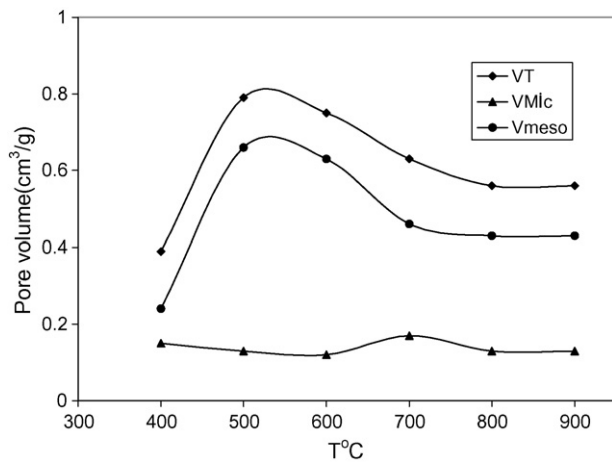

Fig. 4. Micropore, mesopore and total volumes of activated carbons as a function of activation temperatures.

3.3. The structure characterization of AC samples

FT-IR spectrum of starting material and activated carbons (ACs), which were obtained with thermal treatment of starting material at the temperatures between 400 and 900 °C,
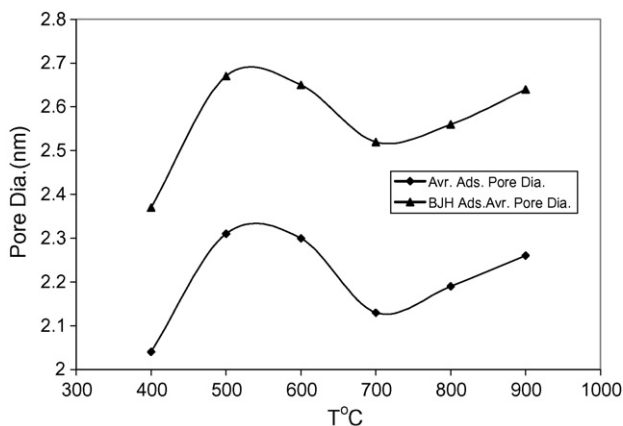

Fig. 5. Influences of activation temperature on the average adsorption pore diameter and BJH adsorption pore diameter.
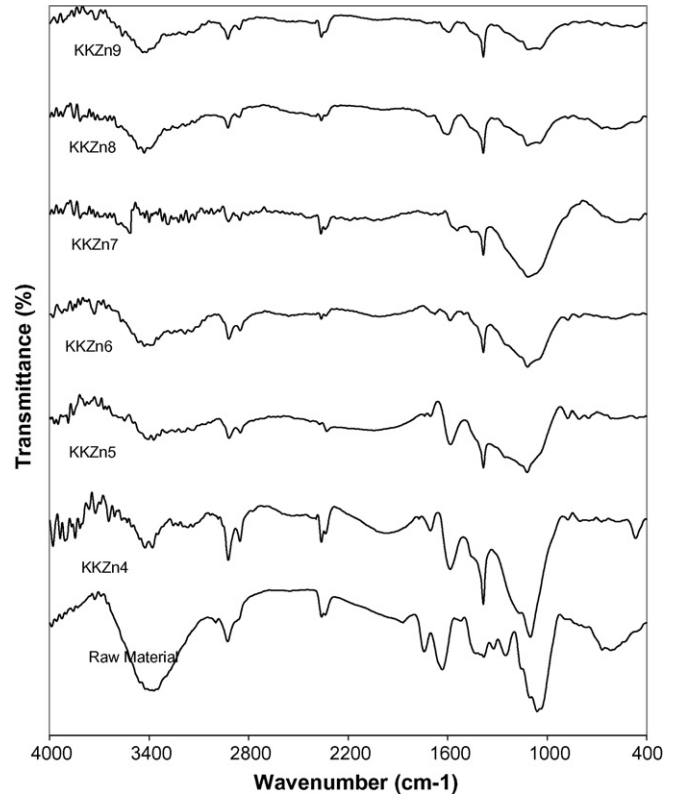

Fig. 6. FT-IR spectra of activated carbon obtained at different activation temperatures.

are presented in Fig. 6. FT-IR spectrum of the starting material shows many peaks belonging different functional groups. The wide peak, which appears between 1000 and 1150 cm^{-1}, is related with ash composition and side peaks at 1109 and 1160–1260 cm^{-1} belong to alcholic and phenolic groups. The small peaks at 1332, 1390 1415 and 1440 cm^{-1} indicate chelat bounded carboxylate structure and these peaks are present in both starting material and AC samples. The peak at 1390 cm^{-1} is relatively small for starting material as compare to AC samples and the intensity of this peak is almost equal for all AC samples, except KKZn4. This peak is not only related with carboxylate groups, but also it could be correlated with aliphatic alkanes depending on arrangement of organic structure in activation process. Existence of the peaks at 2930 and 2950 cm^{-1} in both starting material and ACs supports this idea. The peak at 1630 and 3002 cm^{-1} belong to aromatic C=C and C−H bonds, respectively and they show the existence of aromatic character in raw material. Intensity of this peak is high for KKZn5, but it decreases for the rest of the samples. Elemental analysis results support this observation and hydrogen amount decrease with increasing temperature for the AC samples (71–81%). The amount of carbon increases between 75 and 51% d.b. range as compare to raw material. This indicates formation of graphitic structure in the sample. The peak at 1747 cm^{-1}, which is observed in the raw material and KKZn4, belongs to CO group and it is removed from the structure with thermal treatment at higher temperatures. N, S and especially O content of AC samples decrease dramatically with thermal treatment and this shows
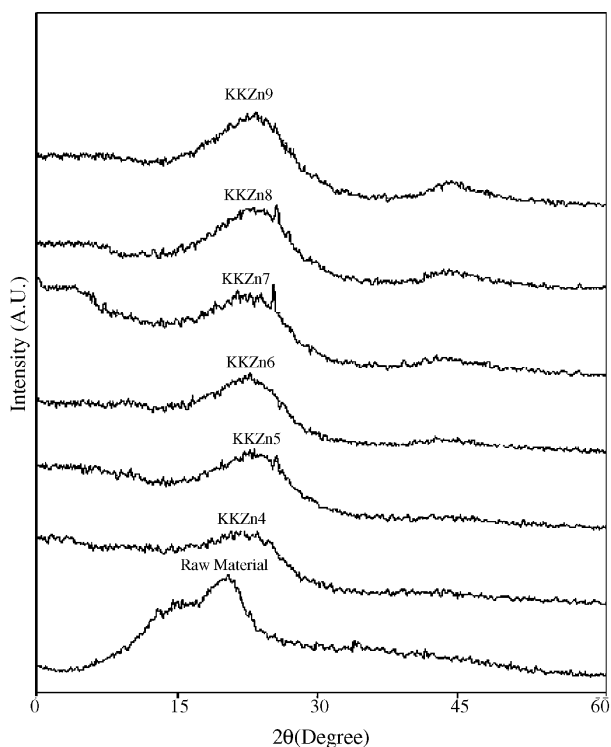
Fig. 7. X-ray diffraction patterns of activated carbon samples.

Fig. 8. DTA curves of activated carbons.

the decreasing in functionality in the main matrix. The wide peak located between 3100 and 3600 cm^{-1} belongs to phenolic OH groups and the intensity of this peak decreases with formation of AC. This is another evidence of functionality loss in AC samples. The peaks, which are located between 900 and 1200 cm^{-1}, represent the ash content in the structure and the ash content of the AC samples is very low. This shows that these peaks could be belong to phenolic and alcoholic OH groups besides ash. In addition to decrease in functionality, decrease in peak's with and peak's height with increasing temperature indicates that this could be caused from mineral content of sample. Activation mechanism of ZnCl$_2$ will be explained separately after performing a detailed investigation [21,22].

XRD diffractograms of raw material and AC samples were shown in Fig. 7. Except raw material, XRD diffractograms of AC samples are similar to each other. Raw material shows amorphous character in wide 2θ ranges. AC samples have amorphous structure between 2θ = 20 and 30 ranges [23,24].

Fig. 8 shows DTA spectrum of raw material and AC samples. Degradation of the structure starts at 250 °C and it ends at 375 °C. The six exothermic peaks in this temperature range show that the samples have a complicated organic structure. The sharp exothermic peaks at 470, 481 and 485 °C indicate that the sample is rich in certain components. All AC samples are generally similar to each other, but start and end-point of the peaks shift to higher values with increasing temperature. The peak located between 400 and 600 °C is present in both raw material and AC samples and it shows that original structure is reserved in AC samples. Comparison of DTA and FT-IR results indicates that start-temperature of the peaks increases with decomposition of functional groups in the structure. According to FT-IR results,
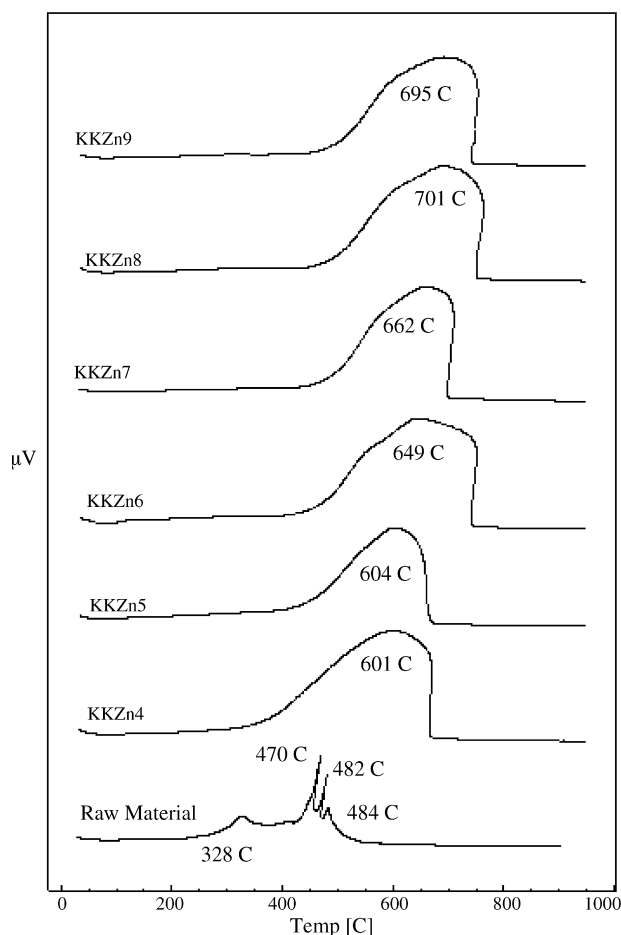
the peaks at 1700–1639 cm^{-1} can be clearly seen for KKZn4 and KKZn5, but they disappear completely for the rest of the samples. Similarly, aliphatic C–H groups have high intensity for KKZn4, but its intensity is low for the rest of the samples. This shows that decomposition of structure belonging this peak starts at 375 °C and ends at 425 °C. If the mid-point of exothermic peaks are compared, it shows that these values increase to higher temperatures with increasing activation temperature [11,25].
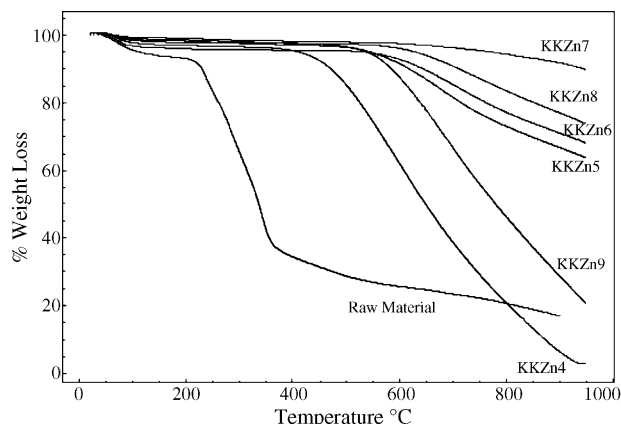

Fig. 9. Thermogravimetric curves of activated carbons.

TGA spectrums of raw material and AC samples are presented Fig. 9. TGA spectrums of all samples have the same characteristic in general. Weight loss of the raw material is 58%. Weight loss of the thermally treated samples decreases between 400 and 700 °C and it starts to increase after 800 °C (KKZn4: 92.4%; KKZn5: 34%; KKZn6: 26%; KKZn7: 9%; KKZn8: 24%; KKZn9: 74%). The biggest difference between weight loss of the samples is observed between 400 and 500 °C. TGA results are in harmony with DTA results and it shows that activation property of $ZnCl_2$ is especially evident at 500 °C [11,25].

4. Conclusion

Activated carbons have been prepared from sugar beet bagasse by chemical activation with $ZnCl_2$. The determined surface area of the activated carbons was 1697 m^2/g at 500 °C. These activated carbons are essentially microporous. Increase in the activation temperature up to 500 °C leads to development of microporous structure and mesoporous structure starts to develop after this temperature. The maximum activation yield is observed as 37% at 500 °C. The yields of the chars, which impregnated with $ZnCl_2$, change scarcely in the temperature range of 600–900 °C. In this temperature range; the surface area and pore volume of the activated carbon decrease. This decrease appears to be due to heat shrinkage. XRD analyses show that AC samples have generally graphitic structure. FT-IR spectrum of starting material shows many peaks belonging different functional groups. The mid-point of exothermic peaks in DTA spectrum increase to higher temperatures with increasing activation temperatures. TGA spectrum of starting material and AC samples show that weight loss of thermally treated sample decreases between 400 and 700 °C and increases between 800 and 900 °C.

Acknowledgement

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