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The effect of activation temperature on properties of activated carbon prepared from wine industry pressing waste

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ABSTRACT

Activated carbons have been widely used as adsorbents in the separation and purification processes for gaseous or aqueous solution system, and they have been also used as a catalyst or a catalyst support in the catalytic processes. Its textural and surface properties depend on the raw material and the method used in its preparation. In this study, activated carbons were prepared by chemical activation with $ZnCl_2$ by using the wine industry pressing waste (grape pulp) as raw material. The influence of activation temperature on the yield, BET surface areas, pore volumes and sizes of the activated carbons were investigated. For this purpose, the wine industry pressing waste was activated at temperatures ranging from 600°C to 800°C, with heating rate of 5°C min^{-1} and impregnation ratio of 1:1 ($ZnCl_2$:grape pulp) under nitrogen atmosphere. The results showed that the activated carbon yield and quality depend principally on the applied temperature where the activation at 700°C resulted in an activated carbon with higher BET surface area (727.10 m^2 g^{-1}) in comparison with the grape pulp (not detected). As a result, the wine industry pressing waste (grape pulp) could be effectively used as a raw material for the preparation of activated carbon.

Keywords: Wine industry pressing waste; Activated carbon; Zinc chloride; Activation temperature

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1. Introduction

Activated carbons having high surface areas have been used in many applications such as wastewater treatment, the removal of harmful gases in the air, solvent recovery, color removal, and ground water improvements [1]. Thus an activated carbon has played an important role in the chemical, pharmaceutical and food industries [2]. Its textural and surface properties depend on the raw material and the method used in its preparation. Activated carbons are generally produced by using relatively expensive carbonaceous materials which are high in carbon but low in inorganic compound. In order to reduce the cost of the activated carbon, cheaper and readily available precursors such as agricultural and agro-based by-products or waste have been tried recently [3–6]. Agricultural wastes are considered to be a very important precursor since they are renewable sources and low cost materials. A variety of agricultural by-products such as sugar beet bagasse [7], sour cherry stones [2], olive bagasse [8], pomegranate seeds [9], grape stalk [6] and rice husk [10], have been reported to be suitable precursors for the production of activated carbon due to their high carbon and low ash contents. Nowadays, activated carbon can be produced through physical and chemical activation. There are two significant advantages of chemical activation in compare with the physical activation. One is the lower temperature in which the process is accomplished. The other is that the global yield of the chemical activation trends to be greater since burn-off char is not required [2,5–6]. In the chemical activation, a raw material is impregnated with an activating reagent and the impregnated material is heat-treated under an inert atmosphere. The common chemical activating agents used in industrial application are $ZnCl_2$, H_3PO_4, KOH and NaOH; and among these agents, zinc chloride is the most widely used chemical in the preparation of activated carbon [3,11,12]. Knowledge of different variables during the activation process is very important in developing the porosity of carbon sought for a given application. Impregnation with $ZnCl_2$ causes degradation of the cellulosic material and dehydration. These

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processes result in charring and aromatization of the carbon skeleton and creation of the pore structure [4]. Chemical activation by $ZnCl_2$ improves the pore development in the carbon structure and because of the effect of the chemicals; the yields of carbon are usually high [2,13].

The most important characteristics of an activated carbon are its surface area and adsorption capacity, which are highly influenced by preparation conditions of the activated carbon. Preparation variables such as activation temperature, activation time and chemical impregnation ratio influence the pore development and surface characteristics of the activated carbon. Therefore, the challenge in activated carbon production is to produce very specific carbons which are suitable for certain applications [2–5,11,14].

Grape is a non-climacteric fruit that grows on the perennial and deciduous woody vines of the genus Vitis. Grapes can be eaten raw or used for making jam, juice, jelly, vinegar, wine, grape seed extracts, raisins, and grape seed oil. Approximately 71% of the world grape production is used for wine, 27% as fresh fruit, and 2% as dried fruit. Wine industry pressing waste, which generates 20% of the total by products of grape industry, is the main residue of wine production. These wastes are composed mainly of stems (25%), skins (25%) and seeds (50%), while the exact distribution of these components depends on several factors [15]. Although these wastes are not intrinsically hazardous, they have to be landfill disposed, incinerated or biologically treated, therefore causing an economical and environmental problem [16]. Turkey is one of the main producers of grape in the world. Grape was cultivated in the area of 4,622,959 decares and 3,650,000 tons of grape was produced in 2015 in Turkey (Turkstat, 2015). Although there are few researches [6,16–19] concerning the usage of the grape industry processing waste as a raw material in the production of activated carbon by physical and chemical activation methods, it is a common industrial byproduct in various countries; therefore it may be a promising candidate as a new resource [17].

Therefore, this study has focused on the production of activated carbon from wine industry pressing waste (grape pulp) by chemical activation with $ZnCl_2$. The effects of the activation temperature on the product yields and pore structures (specific surface area, pore volume, and pore size distribution) of the activated carbons were investigated.

2. Materials and methods

2.1. Materials

Grape pulp was supplied by the Doluca Wine Factories Ind. Inc. (Tekirdag, Turkey), and it was first air dried, then crushed and finally sized, the fraction of particle sizes between 1 and 2 mm was chosen for subsequent studies. All chemical reagents used in this study were of analytical grade. The main characteristics of the grape pulp were given in Table 1.

2.2. Preparation of activated carbon

In this study, chemical activation of grape pulp was performed using $ZnCl_2$. The impregnation ratio was calculated as the ratio of the weight of the grape pulp to the weight of $ZnCl_2$ in solution. The grape pulp was mixed with $ZnCl_2$, in a ratio of 1:1 for $ZnCl_2$:grape pulp mass. Carbonization of the impregnated sample was carried out in tubular reactor (Protherm PTF 12) under nitrogen flow. About 10 g of the impregnated sample was placed on a ceramic crucible in the reactor and heated up to the final carbonization temperature under the nitrogen flow (≈200 cm^3 min^{-1}) at heating rate of 5°C min^{-1} and held for 2 h at this temperature. The final carbonization temperature was varied from 500°C to 800°C. The remain solid after carbonization was mixed with 100 mL of 1 N HCl solution and boiled at about 100°C for 60 min to leach out the activating agent. Then it was filtered and rinsed by warm distilled water several times until the pH value of 6–7. Finally, it was dried at 105 ± 3°C for 24 h, and weighed. The yield of activated carbon was calculated from the following equation:

Table 1
Proximate analysis of grape pulp

Characteristics	Grape pulp
Moisture (wt%)	7.21
Proximate analysis (dry, wt%)	
Volatile Matter	65.10
Ash	6.16
Fixed Carbon*	28.74

*By difference.

$$\text{Yield of activated carbon}(\text{wt\%}) = \frac{\text{Final weigth of activated carbon}}{\text{Initial weigth of impregnated sample}}*100 \tag{1}$$

2.3.Characterization of grape pulp and activated carbon

The contents of ash, moisture and volatile matter of grape pulp were determined according to the methods of ISO R 749, ISO R 771 and ASTM E 872, respectively. The fixed carbon content was determined by subtracting the percentages of, volatile matter, and ash from a sample.Thermogravimetric analysis (TG/DTG) of grape pulp was performed in a NETZSCH STA449 F1 apparatus under nitrogen atmosphere, heated from room temperature to 900°C with a rate of 10°C min^{-1}. The distribution and morphology of the grape pulp and impregnated ($ZnCl_2$) grape pulp were characterized using X-ray diffraction (XRD). The measurements were conducted in a 2θ scan configuration in the range of 10–90° on an X-ray diffractometer (Rigaku D/Max 2200). To determine the surface area of activated carbons, the nitrogen adsorption-desorption isotherms at 77 K were measured by an automated adsorption instrument, Micromeritics Instruments, Tristar II 3020. The surface area was calculated from nitrogen adsorption data by using Micromeritics Instruments software. The adsorption data were obtained over the relative pressure, P/P_0, range from 10^{-5} to 1. The sample was degassed at 300°C under vacuum for 5 h. The apparent surface area of nitrogen was calculated by using the BET (Brunauer–Emmett–Teller) equation within the 0.01–0.2 relative pressure range. Surface functional groups were determined by Fourier transform infrared spectra (FTIR) using

SHIMADZU IR Prestige 21. The surface morphologies were studied by scanning electron microscopy (SEM). The SEM images were performed using JEOL-JSM-6060LV Scanning Electron Microscope.

3. Results and discussion

3.1. Characterization of grape pulp

The results of proximate analysis of the grape pulp are given in Table 1. As can be seen from the table, the grape pulp contained 6.16 wt% of ash, 65.10 wt% of volatile matter and 28.74 wt% of fixed carbon. The volatile matter content of the grape pulp was high (65.10 wt%) however the pulp could be used as precursor for activated carbon production, as it was the case of this work. Also, the acceptable ash content of the grape pulp indicated that it was a suitable precursor for activated carbon production [1,20]. Since the BET surface area of grape pulp was below the detection limit of instruments (Micromeritics Instruments, Tristar II 3020), it could not be determined. Fig. 1 gives the TG/DTG curve for carbonization of grape pulp. The weight loss at the beginning of the process (from 50°C to 240°C) was due to the evaporation of free moisture content. With further increases in temperature, bound water in grape pulp also evaporated. Sharp decrease in weight evidenced at temperatures between 240 and 460°C was caused by the release of volatile matter from grape pulp while above 460°C, decomposition of some structure within grape pulp still took place. A similar trend has been observed for TG/DTG analysis of loquat stones [21] and durian shell [22] that were used as precursor material for activated carbon production. Based on the thermogravimetric analysis of grape pulp, it was decided to produce activated carbon from this raw material by activation at four different final temperatures—500, 600, 700 and 800ºC—to verify which temperature would provide the best yield of activated carbon and the activated carbon with the highest fixed carbon content.

Fig. 2 shows the XRD diffraction profiles of the grape pulp and impregnated ($ZnCl_2$) grape pulp sample. X-ray diffractometer (XRD) method provides general insight about sample whether it has amorphous and/or crystalline structure which means aligned ordered configuration. Additionally, significant data were acquired about the compound of inorganic material in the structure through XRD [23,24]. The grape pulp had a poorly organized configuration with no indication of specific crystalline structure probably due to the various organic impurities and volatile matters present within the structure. This spectrum showed weak peaks that proved the grape pulp has an amorphous structure [25,26]. It has been known that inorganic compounds could be turned into soluble salts by $ZnCl_2$ in the impregnation processes performed with $ZnCl_2$ [23]. ZnO could be identified from the profiles by peak matching. When XRD result of impregnated grape pulp was examined, the peaks that supported the existence of zinc were seen in the mixtures. Notable peaks were determined in the XRD spectrum of mixtures at the levels of 2θ 38.20° and 44.42°, which indicated the presence of ZnO [24]. Upon adding $ZnCl_2$, the amorphous structure of the grape pulp was changed into a crystal structure.

3.2. Yield of activated carbon

The product yield is an important measure of the feasibility of preparing activated carbon from a given precursor. Activation temperature plays an important role on the yield of activated carbon. The effects of the activation temperature on the yields of activated carbon are shown in Fig. 3. It was found out that with increasing activation temperature, the activated carbon yields decreased for constant impregnation ratio ($ZnCl_2$:grape pulp) of 1:1 (wt%). When the activation temperature increased from 500°C to 800°C, the activated carbon yield decreased from 25.60% to 17.45%. With increasing activation temperature, the yield of activated carbon decreased as the weight loss rate is higher primarily due to initial large amount of volatiles that can be easily released with higher temperature as well as the

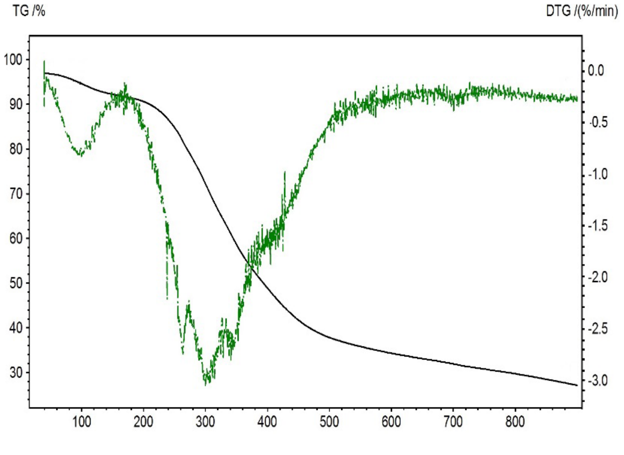

Fig. 1. TG-DTG graphs of the grape pulp.

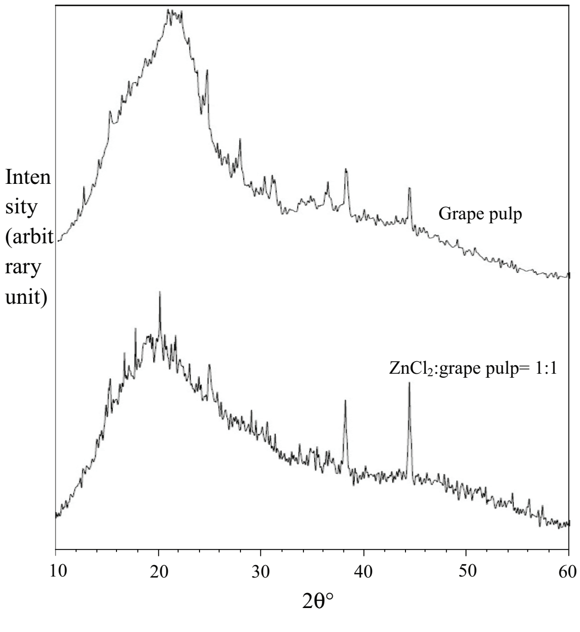

Fig. 2. XRD diffraction profiles of grape pulp and impregnated ($ZnCl_2$) grape pulp.

loss of moisture to a lesser extent [2,14]. Similar results were reported in related literature [20,21,27,28]. The results showed that the activation temperature had a significant effect on the final yield of activated carbon.

3.3. Surface properties of activated carbons

In the chemical activation, the final activation temperature is important process parameters in determining the surface area and the pore volume of the activated carbon [1–5,18]. The effects of activation temperature on the surface areas (BET, micropore and mesopore) and pore volumes (total, micropore, and mesopore) of the activated carbons are shown in Table 2. When the activation temperature increased from 500°C to 700°C, BET surface areas and pore volumes increased significantly and reached to the maximum value (727.10 $m^2 g^{-1}$ and 1.826 $cm^3 g^{-1}$). This phenomenon was due to the release of the volatile matters. However, at a relatively higher temperature (800°C) the trend was reversed. The continual decrease in these properties with increasing the temperature from 700°C to 800°C was probably caused by the sintering effect of the volatiles and the shrinkage of the carbon structure, resulting in the narrowing and closing up to some of the pores [1–4,20,22].By increasing temperature, structural ordering, pore widening and/or the coalescence of neighboring pores seem to predominate, leading to a decrease in the pore volume and surface area [29]. It was also showed that activated carbons prepared at activation temperature of 700°C and at impregnation ratio of 1:1 yielded the largest BET surface area and micropore volume.

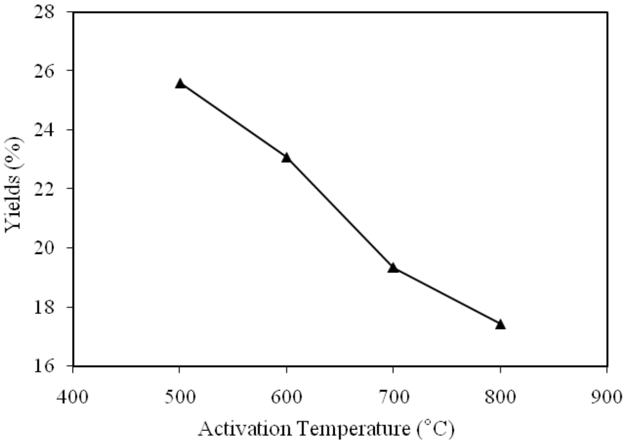

Fig. 3. Effect of activation temperature on the yield of activated carbons for constant impregnation ratio ($ZnCl_2$:grape pulp) of 1:1.

The nitrogen adsorption isotherms and pore size distributions for the activated carbons obtained at various activation temperatures are shown in Fig. 4. The plateau of the isotherms (Fig. 4a) commences at high relative pressures (P/P_0) and toward the end of isotherm, steep gradient exist as a result of a limited uptake of nitrogen, indicating capillary condensation in the mesopore. The adsorption isotherms for the activated carbons have been characterized as Type I isotherm, according to the Inter-

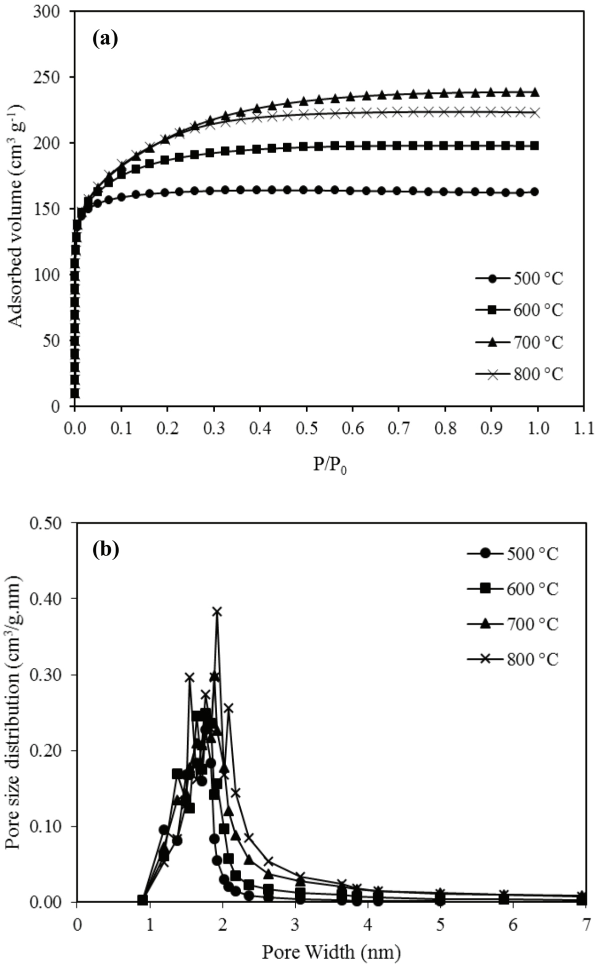

Fig. 4. Nitrogen adsorption isotherms (a) and pore size distributions (b) for activated carbons prepared at different activation temperature.

Table 2
Effect of pyrolysis temperature on surface areas and pore volumes of activated carbon

Pyrolysis temperature (°C)	S_{BET} ($m^2 g^{-1}$)	S_{micro} ($m^2 g^{-1}$)	S_{meso} ($m^2 g^{-1}$)	V_{total} ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_{meso} ($cm^3 g^{-1}$)	S_{micro} (%)	Dp (nm)
500	485.86	430.06	55.80	1.042	0.816	0.226	88.52	1.78
600	590.72	487.08	103.64	1.530	1.276	0.254	82.46	1.69
700	727.10	555.70	171.40	1.826	1.544	0.282	76.43	1.57
800	671.14	601.88	69.26	1.330	1.018	0.312	89.68	1.76

national Union of Pure and Applied Chemistry (IUPAC) classification. This type of isotherm has been attributed to mesoporous and macroporous materials that allowed unrestricted monolayer adsorption to occur at high relative pressure [21,22].These features indicated the development of micro and mesoporous structure in the grape pulp during activation process, further confirmed by the DFT (density functional theory) pore size distributions (Fig. 4b). The structures of the porous activated carbons have been classified into three groups as micropore (<2 nm), mesopore (2–50 nm) and macropore (>50 nm) according to IUPAC [2,20]. The activated carbon produced from grape pulp in this study contained both micropores and mesopores; nevertheless, the micropore volume was larger than the mesopore volume. The average pore diameters of activated carbons varied between 1.57 nm and 1.78 nm, principally denoted microporous characteristics (Table 2) [2,30]. Similar results were obtained for the activated carbons produced from Paulownia [31], cherry stones [2], waste tea [32], pomegranate seeds [9] and olive bagasse [8].

3.4. FTIR analysis

Fourier transform infrared spectra (FTIR) were collected for qualitative characterization of surface functional groups of activated carbons produced by chemical methods. FTIR analyses results of activated carbons obtained at different activation temperatures are given in Fig. 5. The FTIR analyses indicated that the functional groups of activated carbons obtained at different conditions were similar. While the bands at about 2853.48–2922.91 cm^{-1} which were generally attributed to symmetric or asymmetric stretching of aliphatic band in –CH, $-CH_2$ or $-CH_3$ were observed as much stronger at grape pulp, they were not seen in the FTIR spectrum of the activated carbons. [23,33]. It has been reported that the olefinic C=C stretching vibrations absorptions caused the band at about 1607.94 cm^{-1} while the skeletal C=C vibrations in aromatic rings caused another two bands at about 1498.25 and 1412.11 cm^{-1} [9,11,34]. The band at about 1030.77 cm^{-1} has been occurred due to the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters showing C–O stretching and O–H deformation vibrations [2,11]. These bands decreased in activated carbons with increasing temperature at activation process as compared to that of the raw material. This situation could be attributed to the decomposition of cellulose, hemicellulose and lignin in the grape pulp by activation process [2,6].

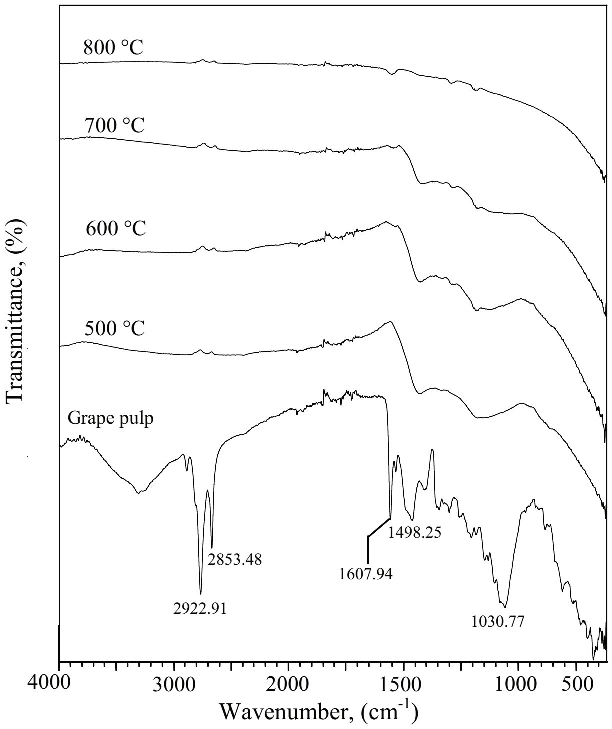

Fig. 5. FTIR spectra of grape pulp and activated carbons obtained at different activation temperatures.

3.5. Scanning electron microscopy

The scanning electron microscopy (SEM) technique was used to observe the surface morphology of the raw material and the prepared activated carbons. Fig. 6 illustrates the SEM photographs of thegrape pulp and activated carbons produced at different activation temperatures. The significant differences were observed between the surface topographies of grape pulp and activated carbons. There were no pores available on the surface of the grape pulp whereas many large pores were developed on the surface of the activated carbons. Due to this well-developed pores, the activated carbons possessed high BET surface area and adsorptive capacity [33]. Depending on the activation temperatures, the external surfaces of the activated carbons had the pores which were at different sizes and different shapes. The SEM images of the activated carbons were analyzed and the pore size was observed to grow with increasing activation temperature from 500 to 700°C. However, at relatively higher activation temperature (800°C), the activated carbons had lower BET surface areas owing to the shrinkage of carbons at post-softening and swelling temperatures, resulting in narrowing or closing pores, as supported by the BET surface area results [34,35]. It seemed that the cavities on the surface of the carbons resulted from the evaporation of $ZnCl_2$ during carbonization, leaving the space previously occupied by the $ZnCl_2$. Therefore, the $ZnCl_2$has been an effective activating agent to obtain activated carbon having high-surface area [35].

4. Conclusions

Activated carbon with high surface area was prepared from grape pulp bu chemical activation process with $ZnCl_2$ (impregnation ratio of 1:1) at different activation temperatures. The experimental results showed that activation temperature was highly effective on the porosity, surface area and pore volume of the activated carbon. It was found that the specific surface area of the activated carbon was 727.10 $m^2\ g^{-1}$ at a carbonization temperature of 700°C ratio of 1:1 for $ZnCl_2$:grape pulp mass. Depending on the activation temperature, the external surfaces

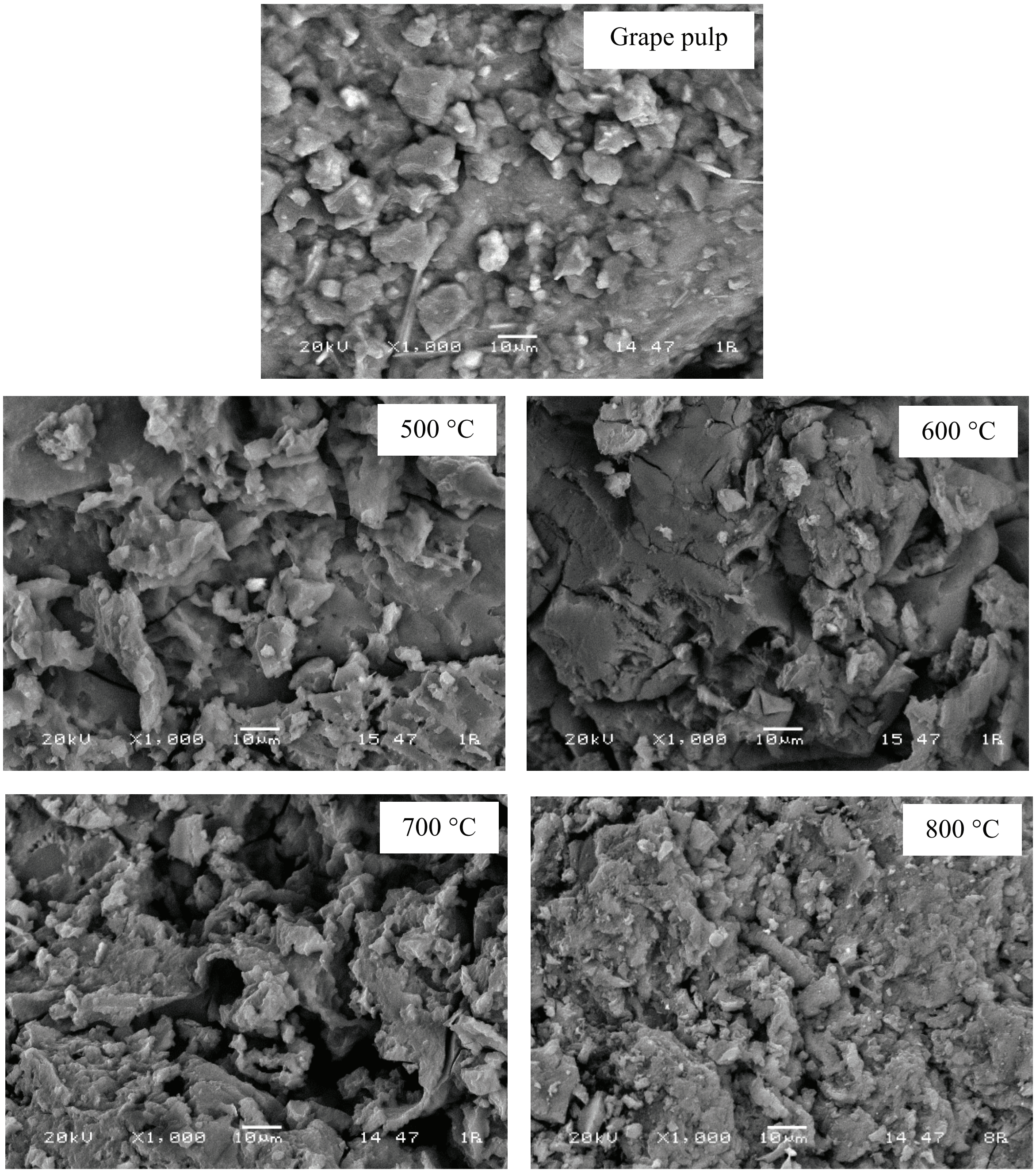

Fig. 6. Scanning electron microscopy images (×1000) of grape pulp and activated carbons obtained at different activation temperatures.

of the activated carbons had the pores which were at different sizes and shapes. The production of activated carbons with high surface area from grape pulp, a waste of wine industry pressing waste, is indeed of importance from the view point of economical and environmental aspects. Also, activated carbon obtained at optimum conditions could be effectively used as adsorbents for various environmental applications such as removing hazardous compounds from industrial waste gases and wastewater.

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