Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption

Hasan Saygili, Fuat Güzel, Yunus Onal

Department of Chemistry, Faculty of Science, Batman University, 72100 Batman, Turkey
Department of Chemistry, Faculty of Education, Dicle University, 21280 Diyarbakir, Turkey
Department of Chemical Engineering, Faculty of Engineering, Inonu University, 44280 Malatya, Turkey

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1. Introduction

Activated carbon (AC) remains one of the most used adsorbents owing to its high specific surface area, favorable pore size distribution and the high degree of surface reactivity (Kaouah et al., 2013). ACs are widely used in various fields such as purification and separation in many industrial processes including medicinal use, gas storage, pollutant, odor removal, gas separation, catalysis, pharmaceuticals, as electrode materials in electrochemical devices and in the wastewater treatment (Şahin et al., 2013). Therefore, the demand for ACs is continuously increasing day by day.

In practice, for the production of commercial ACs two primary sources such as coal and lignocellulosic materials are usually utilized. The composition of the lignocellulosic material regarding the cellulose, hemicelluloses and lignin content determines, to some extent, the porosity development of the produced ACs (Nabaisa et al., 2013). In principle, in the production of ACs, two methods such as physical activation and chemical activation are used. Chemical activation has been of significant research in the recent years, as it offers several advantages compared to the so-called physical activation, e.g., lower temperatures for pyrolysis, high yield, very high surface area, etc. Among the disadvantages of the chemical activation process, the corrosiveness of the process and the washing stage are to be noted. The chemicals used in the chemical activation are alkali (KOH, K2CO3, NaOH and Na2CO3), alkali earth metal salts (AlCl3 and ZnCl2) and some acids (H3PO4 and H2SO4). These chemicals are dehydrating agents that influence pyrolytic decomposition and inhibit the formation of tar. In the case of chemical activation, the effect of KOH and ZnCl2 on the carbonization of precursor has been special interest and ZnCl2 in particular is a widely used chemical agent in the production of AC (Ozdemir et al., 2014). However, commercially available ACs are expensive materials although they had regenerative capacity (Zhao et al., 2012). The most precursors used for the production of ACs are organic materials that are rich in carbon. Agro and natural-wastes
are considered being a very important feedstock for the AC production since they are renewable sources and low-cost materials (Sathishkumar et al., 2012). In recent years, there has been increasing interest in the research on the production of ACs by using renewable and cheaper precursor. Agricultural by-products are the one, which considered being a very important precursor for AC production because there are renewable sources and low-cost materials. Therefore, the abundance and availability of agricultural wastes make them an excellent choice as this will reduce the cost of waste disposal and provide an e solution to environmental problems (Djilani et al., 2012). Lately, a lot of research has been reported on ACs from agricultural wastes, such as *jatropha curcas* pods (Sathishkumar et al., 2012), apricot stones (Şentorun-Shalaby et al., 2006), mehagani sawdust (Santra et al., 2008), coconut shell (Santra et al., 2008), rice husk (Malik, 2003; Santra et al., 2008), buriti shells (Pezoti et al., 2014), pine cone (Duman et al., 2009; Özhan et al., 2014), coffee husks (Oliveira et al., 2009), tea industry waste (Gündoğdu et al., 2013), grape stalk (Özdemir et al., 2014), etc. have been successfully used in the production of ACs. Grape is used in food and wine production industry. Although Turkey ranks fourth with 4 million tons in the world grape production, and in the wine production (about twenty thousand tons) is 38th. According to grape processing industry, weight of fresh grapes arises about 10–20% solid waste (Öndogan et al., 2008). These wastes are mostly evaluated in the food, pharmaceutical and cosmetic industry. To our knowledge, there are no published reports on grape processing wastes (GW) for the AC production.

In this study, we aimed to use as a new precursor in the production of AC, that it has a central place in industrial- and laboratory-scale applications, in addition to other utilization areas of GW. For this, the effects of impregnation ratio of activator to precursor, activation temperature and activation time on the pore characteristics (specific surface area, pore volume, and average pore diameter) were studied in order to obtain large surface area and pore volume of the product. Subsequently, the physicochemical characteristics of the AC obtained under optimum conditions were determined by using some techniques such as proximate-ultimate analysis, derivative thermo-gravimetric (TG/DTA) analysis, nitrogen adsorption-desorption, scanning electron microscopy (SEM), X-ray diffraction (XRD) and surface functional group analysis by Fourier transform infrared spectroscopy (FT-IR), Boehm’s titration method and point of zero charge (pH\text{pzc}). In addition, the optimal AC was tested to remove cationic and anionic dyes from aqueous solutions. Dyes are one of the common pollutants in wastewaters. Over 7 × 10^5 ton/annum and approximately 10,000 different types of dyes and pigments are produced in the world dyes are highly water-soluble and are generally present in the effluents of the textile, leather, dyeing, paper, and dye manufacturing industries (Hejazifar and Azizian, 2012). Dye producers and consumers are interested in the stability and fastness of dyes and consequently, are producing dyestuffs that are more difficult to degrade after being used. It is estimated that 10–15% of the dye is lost during the dyeing process and released with the effluent (Ezgi et al., 2008). Most of the dyes are carcinogenic, mutagenic, and can cause a severe health hazard to human beings. In addition, they impede light penetration into the water, retard photosynthetic activity, and inhibit the growth of biota (Hejazifar and Azizian, 2012). In this study, Methylen blue (MB) and Metanil yellow (MY) were selected as model dyes to evaluate the adsorption performance of optimal AC produced.

2. Materials and methods

In the production of activated carbon, the preparation conditions are important as well as the properties of the precursor used. Therefore characteristics of precursor should be identified and optimum preparation conditions should be determined carefully.

2.1. Ultimate, proximate, component and thermal analyses of the grape waste

GW was collected from a local wine factory in Turkey. It was washed with water to take off impurities and then dried overnight in an oven at 50 °C prior to its chemical activation.

The advantage of the GW for AC production was first checked using various methods such as ultimate analysis, proximate and component analyses. The elemental analysis (C, H, N, and S) was determined with an elemental analyzer (Leco CHNS 932). The proximate analysis was conducted according to ASTM D 3172–3175 test standards and the results were given as moisture, volatile matter, ash, and fixed carbon contents. Similar analyses were performed for the AC produced at optimized conditions. Component analysis including extractives, lignin, hemicelluloses, and cellulose of GW was done according to Technical Association of the Pulp and Paper Industry, (TAPPI) standards; T264 om-88, T222 om-88 and T203 om-83, respectively.

The thermal behavior was measured with TG analyzer (Shimadzu, TGA/DTA-50). About 10 mg of sample material was heated from 25 °C to 900 °C at a ramping rate of 10 K/min under nitrogen gas atmosphere with the low rate of 200 mL/min, until no further weight loss was detected.

2.2. Production of optimal activated carbon

Firstly, GW was heated without the use of chemical agent to examine the effect of chemical activation. The heating was performed in a stainless-steel tubular reactor (7.0 cm diameter × 100 cm length) (Fig. 1) under nitrogen atmosphere (99.99%) flow (100 mL/min) at the rate of 10 °C/min at 600 °C for 1 h.

Subsequently, different impregnation ratios of ZnCl₂ to GW, activation temperatures and times were studied in order to establish the optimal conditions for preparing of ACs with high surface area. For this purpose, the following production steps were viewed: (1) The impregnation ratios were varied from 1:1 to 1:8. The mixtures were then filtered, and the remaining solids were dried at 110 °C for about 24 h. They were activated by keeping at temperature of 500 °C and activation time of 1 h (depending on the impregnation ratio). (2) Then, the activation time of 1 h and impregnation ratio of 1:6 were fixed, and the temperature was varied from 400 to 800 °C (depending on the activation temperature). (3) The activation time was varied from 0.5 h to 4 h (depending on the time) along with the preset values of activation temperature of 600 °C and impregnation ratio of 1:6 in the last step.

After the activation processes, the produced ACs were cooled down to room temperature under nitrogen flow, and 0.2 N HCl was added on to AC. The produced ACs were washed sequentially several times with hot distilled water to remove residual chemical until it did not give Cl⁻ reaction with AgNO₃, and dried at 105 °C for 12 h and then sieved between 177 and 400 μm. They were referred to as AC followed by the impregnation ratio, activation temperature and time; for instance, AC11405 represented impregnation ratio 1/1 for the first two number of 11, activation temperature of 400 °C for the third number of 4, and activation for 0.5 h for last 05. The yield was calculated as the ratio of the dry weight of produced AC to the weight of the air-dried of the raw precursor.

In this work, efficiency and quality of the produced ACs were preliminarily characterized by measuring some textural properties...
such as the BET (Brunauer-Emmett-Teller) surface area, pore volume, mesoporosity, microporosity and average pore diameter.

2.3. Characterization of optimal activated carbon

Textural characteristics were determined by nitrogen adsorption at 77 K with an automatic adsorption instrument (Micromeritics, ASAP 2020). The BET surface area ($S_{\text{BET}}$), total pore volume ($V_T$) and pore size distribution were determined from nitrogen adsorption-desorption data by using Quantachrome software. The micropore volume ($V_{\text{mic}}$) was determined by using the t-plot method. The mesopore volume ($V_{\text{mes}}$) was determined by subtracting the $V_{\text{mic}}$ from the $V_T$ while the microporosity ($V_{\text{mic}}(\%)$) and mesoporosity ($V_{\text{mes}}(\%)$) were based on the $V_T$. The surface morphologies were examined by using SEM technique (JEOL JSM-6335F). Surface functional groups were detected using the pressed potassium bromide (KBr) pellets containing 5% of carbon sample by FT-IR spectrometer (Perkin Elmer spectrum 100) in the scanning range of 4000–650 cm$^{-1}$. The XRD patterns were collected on an X-ray powder diffractometer (Bruker, D8 Discovery EVA).

The quantitative determination of the acidic and basic functional groups on the surface was done according to the Boehm’s titration method (Boehm et al., 2002). This method allows modeling the principal acidic oxygenated functions of the AC such as carboxylic acids, lactones and phenols using bases of increasing strength as NaOH and HCl, respectively that reacted with the optimal AC. The point of zero charge ($pH_{\text{pzc}}$) is a very important parameter characterizing the acid-base behavior of the solids. The $pH_{\text{pzc}}$, i.e., pH of the point zero charge was measured (Chan et al., 2011). The surface is negatively charged at $pH > pH_{\text{pzc}}$, and positively charged at $pH < pH_{\text{pzc}}$ (Babic et al., 1999). It was determined by the method described by Preethi and Sivasamy (Preethi and Sivasamy, 2006). The pH was measured by using the modifying method of the ASTM 3838, named Standard Test Method for pH of AC. Cation exchange capacity (CEC) which is a scale to reversibly adsorb positively charged species of optimal AC was determined by the method described by Puziy et al. (Puziy et al., 2002).

2.4. Adsorption performances and isotherm modeling

The basic dye, MB (Type: cationic, chemical formula: C$_{16}$H$_{18}$ClN$_3$S, $M_w$: 319.85 g/mol, color index: basic blue 9, $\lambda_{\text{max}}$: 665 nm) and acidic dye, MY (Type: anionic, chemical formula: C$_{18}$H$_{14}$N$_3$NaO$_3$S, color index: acid yellow 36, $\lambda_{\text{max}}$: 433 nm, $M_w$: 375.38 g/mol) were used as adsorbates. These were purchased from Sigma–Aldrich Company. Stock dye solutions (1000 mg/L) were prepared by dissolving 1 g of dye in 1 L of double distilled water. Experimental solutions of desired concentration were obtained by further dilution.

For adsorption study of dyes used, a constant mass of produced optimal AC (30 mg) was weighed into 100 mL Erlenmeyer flasks and contacted with 50 mL of each dye solutions of different initial concentration from 200 to 900 mg/L at natural pH (6.33 for MB; 6.23 for MY) in aqueous solutions of used dyes. The samples were shaken mechanically at 120 rpm in a water bath shaker (Daihan-WSB-30, Korea) and kept at a temperature of 30 °C for a period of approximately 24 h, which is enough for guaranteeing adsorption equilibrium for both dye onto surface. After each adsorption process, the samples were filtrated for solid—liquid separation and the residual concentrations of MB and MY were analyzed by a UV—vis spectrophotometer (Perkin Elmer-Lambda 25) at 665 and 433 nm maximum wavelengths, respectively. The amount of dye adsorbed onto per gram of adsorbent ($q_e$) was calculated by using Eq. (1):

$$q_e = \frac{(C_0 - C_e) V}{m}$$ (1)

where, where $C_e$ (mg/L) is the solute equilibrium concentration in the liquid phase; $C_0$ (mg/L) is the initial concentration of the solute in the solution; and $V$ (L) is the volume of adsorbate solution and $m$ (g) is the mass of adsorbent. Each experiment was carried out in duplicate, and the average values are given.

A number of isotherms have been developed to describe equilibrium relationships. For the isotherm modeling, two famous isotherm models, namely the Freundlich (Freundlich, 1906) and the Langmuir (Langmuir, 1918) isotherm models were used to the equilibrium data obtained. The used linearized isotherm equations were (Ahmed and Theydan, 2012):

Freundlich isotherm

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$ (2)

Langmuir isotherm

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e$$ (3)

where $K_F$ (L/g) and $n$ are the Freundlich adsorption constants, and $1/n$ is a measure of the adsorption intensity. $q_m$ (mg/g) is the
Langmuir maximum adsorption capacity of adsorbate per unit mass of adsorbate, and expressed as $q_{m,Mb}$ for MB and $q_{m,MY}$ for MY. $b$ (L/mg) is the Langmuir equilibrium constant related to the energy of adsorption. Isotherm parameters and correlation coefficients ($R^2$) were obtained by using Microsoft Office Excel 2007 software. The higher the value of $R^2$ the more accurate is the model that predicts the experimental data. The degree of suitability of the produced optimal AC towards used dyes was estimated from the values of the separation factor ($R_L$) using the following relation (Qi and Xu, 2004):

$$R_L = \frac{1}{1 + bC_0}$$

$R_L$ indicates the type of isotherm to be reversible ($R_L = 0$), favorable (0 < $R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

3. Results and discussion

In this section, the properties of GW, the effect of conditions in the production of optimal AC and also the textural and adsorption properties of the AC produced in optimal conditions were examined.

3.1. Ultimate, proximate, component and thermal analysis of the grape waste

The proximate, ultimate and component analysis results revealed that GW contains 38.28% holocellulose (32.96% cellulose + 5.32% hemicellulose), 52.64% lignin, 9.08% extractives, 8.74% moisture, 71.16% volatile matter, 17.96% fixed carbon, 2.14% ash, 49.46% carbon, 5.56% hydrogen and 43.53% oxygen as expected for most lignocellulosic material. Although GW has very high volatile content, low ash content and a reasonable amount of carbon makes it a suitable precursor.

In order to determine the thermal behavior of the GW during the activation, the sample was subjected to TG/DTA analysis (Fig. 2). TG curve displays a weight loss in the temperature range of 50–190 °C due to dehydration of the sample. 8.12% weight loss was determined at this temperature range. This value is close to the moisture percentage (8.74%) of the GW. The highest weight loss was observed between 240 and 550 °C, which indicates the thermal decompositions of the cellulose, hemicelluloses and lignin. In this range, the weight loss is about 52%. Above 550 °C, the weight loss was small thus indicating that the basic structure of the char has been formed approximately at this temperature. At the temperatures above 550 °C were not observed significantly lose in weight. Therefore, this temperature can be said to be the lowest activation temperature for AC production. In the DTA spectrum in Fig. 2, the endothermic peak around 105 °C, belongs to the removal of water. The weak endothermic peak around 400 °C belongs to hydroxyl deformation (Yang et al., 2007).

Table 1

<table>
<thead>
<tr>
<th>Impregnation ratio (ZnCl2/GW, w/w)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Sample ID</th>
<th>Textural characteristics</th>
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<tbody>
<tr>
<td></td>
<td>SBET (m²/g)</td>
<td>Vt (cm³/g)</td>
<td>Vmic (%)</td>
<td>Vmes (%)</td>
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<tr>
<td>1.0</td>
<td>500</td>
<td>1.0</td>
<td>AC151</td>
<td>912</td>
</tr>
<tr>
<td>2.0</td>
<td>500</td>
<td>1.0</td>
<td>AC251</td>
<td>1015</td>
</tr>
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<td>4.0</td>
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<td>1.0</td>
<td>AC451</td>
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<tr>
<td>6.0</td>
<td>500</td>
<td>1.0</td>
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<td>500</td>
<td>1.0</td>
<td>AC851</td>
<td>1231</td>
</tr>
<tr>
<td>6.0</td>
<td>400</td>
<td>1.0</td>
<td>AC641</td>
<td>819</td>
</tr>
<tr>
<td>6.0</td>
<td>600</td>
<td>1.0</td>
<td>AC661</td>
<td>1455</td>
</tr>
<tr>
<td>6.0</td>
<td>800</td>
<td>1.0</td>
<td>AC681</td>
<td>988</td>
</tr>
<tr>
<td>6.0</td>
<td>600</td>
<td>0.5</td>
<td>AC6605</td>
<td>890</td>
</tr>
<tr>
<td>6.0</td>
<td>600</td>
<td>2.0</td>
<td>AC662</td>
<td>914</td>
</tr>
<tr>
<td>6.0</td>
<td>600</td>
<td>4.0</td>
<td>AC664</td>
<td>911</td>
</tr>
</tbody>
</table>
carbonization, a dehydration of the raw material occurs, which results in charring and aromatization of the carbon skeleton and creation of the porous structure (El-Hendawy et al., 2001). As seen from this figure, while impregnation ratio increased from 1:1 to 1:6, the $S_{\text{BET}}$, $V_T$, $V_{\text{mes}}$(%), $D_p$(nm) values increased from 911 to 1361 m²/g, from 0.608 to 2.0 cm³/g, from 32.07% to 82.85% and from 2.40 to 6.33 nm, respectively, and $V_{\text{mic}}$(%) decreased from 67.93% to 17.15%. From these results, it is understood that zinc chloride impregnation ratio significantly affect to porosity. With low impregnation ratio, due to the effect of ZnCl₂, the formation of tar is inhibited and the release of volatiles is promoted, producing more micropores. But at higher impregnation ratio, the more swelling impregnated precursor material and stronger release of volatiles in the activation process will lead to the widening of pores; micropores formed are subsequently converted to mesopores (Yang and Qiu, 2011). ZnCl₂ activation effect can be seen from the elemental analyzes results. The elemental analysis results of GW and produced AC showed that the carbon contents increased from 17.96% to 81.76% whereas amounts of hydrogen and oxygen decreased from 5.56% to 2.71% and from 43.53% to 14.45%, respectively, with the influence of ZnCl₂ activation. This could be attributed to the fact that ZnCl₂ selectively extracted H and O away from the GW rather than AC. This causes eventually to an increase in the surface area and porosity (Özdemir et al., 2014).

As seen from the Fig. 4(A) (a-d), the maximum values of $S_{\text{BET}}$ (1361 m²/g), $V_T$ (2.0 cm³/g), $V_{\text{mes}}$ (82.85%) and $D_p$ (6.33 nm) could

Fig. 3. Nitrogen adsorption (filled symbols)-desorption (empty symbols) isotherms and pore size distribution (inset) for activated carbons produced from GW at the different impregnation ratios (a), activation temperatures (b) and activation times (c).
Fig. 4. Effects of impregnation ratio (A), activation temperature (B) and activation time (C) on the surface areas (a), pore volumes (b), porosities (c) and average pore diameters (d).
be accessed at impregnation ratio of 6:1, and above 6:1 these values decreased. Hence, it was chosen as the optimum impregnation ratio for use in subsequent experiments.

3.2.2. Effect of activation temperature

Activation temperature is one of the most important process factors affecting the textural properties of the ACs. The production of ACs was carried out at different temperatures to be activated for the time of 1 h by keeping the impregnation ratio at 6:1. As seen from the Fig. 4(B)(a-d), while temperature increased from 400 to 600 °C, the \( \text{SBET} \), \( \text{Vf} \), \( \text{Vnec}(\%) \) and \( \text{Dp}(\text{nm}) \) values increased from 899.40 to 1455 m\(^2\)/g, from 0.556 to 2.318 cm\(^3\)/g, from 78.57% to 94.61% and from 5.63 to 6.81 nm, respectively, and \( \text{Vmic}(\%) \) decreased from 25.36% to 5.39%. This is due to the formation of new pores with continuing of the evaporating agents resulting from the decomposition of primary compounds of the GW with increasing of temperature, and above 600 °C decreased. This decrease may be due to narrowing of the pores with increase in temperature (Hayashi et al., 2000; Deiana et al., 2009).

3.2.3. Effect of activation time

Activation time is another factor affecting the textural properties of the ACs. The production of ACs was carried out at different activation time (0.5–4 h) to be activated for 600 °C by keeping the impregnation ratio at 6:1. As seen from the Fig. 4(C)(a-d), while the time increased from 0.5 h to 1 h, the \( \text{SBET} \), \( \text{Vf} \), \( \text{Vnec}(\%) \) and \( \text{Dp}(\text{nm}) \) values increased from 899.40 to 1455 m\(^2\)/g, from 0.556 to 2.318 cm\(^3\)/g, from 78.57% to 94.61% and from 5.63 to 6.81 nm, respectively, and \( \text{Vmic}(\%) \) decreased from 21.43% to 5.39%. However, while the activation time increased from 1 h to 4 h, the \( \text{SBET} \), \( \text{Vf} \), \( \text{Vnec}(\%) \) and \( \text{Dp}(\text{nm}) \) values decreased. This decrease was probably because the excessive time leaded to the collapse of pores, so the surface area and pore volume became smaller (Wang et al., 2011). Therefore, it can be stated that the carbonization time of 60 min is more suitable to produce optimal AC from the GW activated by ZnCl\(_2\).

3.2.4. Process optimization

The above-mentioned production conditions were chosen to obtain best textural characteristics, in particular \( \text{SBET} \) and \( \text{Vf} \) values. From the textural characteristics in Table 1, the optimal AC (AC661) which had the highest \( \text{SBET} \) (1455 m\(^2\)/g), \( \text{Vf} \) (2.318 cm\(^3\)/g), \( \text{Vnec}(\%) \) (94.61%) and \( \text{Dp}(6.81 \text{ nm}) \) was obtained by these conditions as follows: 6:1(w/w) ZnCl\(_2\) to GW ratio, 4 h activation time for use in subsequent experiments.

3.3. Characterization of the optimal activated carbon

The proximate and ultimate analysis results related to the GWAC are given in Table 2. It can be seen that the contents of carbon and ash increased, in the GWAC, whereas the contents of hydrogen, nitrogen, oxygen and sulfur decreased. This is due to the release of volatiles during activation, which can result in the elimination of the non-carbon species. The proximate analysis indicates an increase of fixed carbon percentage in GWAC than in the GW. This may be because of conversion of volatile matter of sludge into fixed carbon during activation. The GWAC also possessed a low concentration of ash (14.23%) indicating a high-quality carbon adsorbent. Low ash content typically leads to superior adsorption of organic compounds from aqueous solution due to the hydrophobicity of the material (Suzuki, 1990). Because of this feature of GWAC, the removal efficiency of dye is strengthened to be high.

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
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<td>Moisture</td>
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<td>Fixed carbon</td>
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<td>Yield</td>
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<td>Sulfur</td>
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<td>Burn-off</td>
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<table>
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<th>Parameter</th>
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<tbody>
<tr>
<td>( \text{SBET} ) (m(^2)/g)</td>
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<tr>
<td>( \text{Vf} ) (cm(^3)/g)</td>
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<td>( \text{pH}_{\text{HNO}_3} )</td>
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</table>

* (dry basis, wt %).

The nitrogen adsorption-desorption isotherms (inset) as well as the pore size distributions for the GWAC is illustrated in Fig. 3(c). The shape of its N\(_2\) adsorption-desorption isotherm was a mixture of types I and IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Sing et al., 1985), with a wider hysteresis loop at high relative pressures, suggesting that GWAC has a mixed microporous and mesoporous structure. The textural characteristics of GWAC obtained from the nitrogen adsorption-desorption isotherms were listed in Table 2. As seen from this table, the GWAC contains both micropores and mesopores; nevertheless, the mesopore volume is larger than the micropore volume. Pore size distribution, a very important property of adsorbents, determines the fraction of the total pore volume accessible to molecules of a given size and shape, and also this is one of the criteria by which carbon adsorbents are selected for a particular application. This study assumes that micropores are less than 2 nm wide, mesopores are 2–50 nm wide and macropores are more than 50 nm wide (Sing et al., 1985). Fig. 3(c) presents the pore size distribution for the GWAC. As seen this figure, the dominant pore of GWAC is in the range of 5–35 nm, and its average pore diameter is 6.81 nm. Therefore, GWAC is typically mesoporous. This can be also concluded from the results of Table 2, which show a mesopore volume of 2.193 cm\(^3\)/g compared to a micropore of 0.125 cm\(^3\)/g. These results indicate that a significant amount of mesoporosity (94.61%) and a certain amount of microporosity (5.39%) were formed in the GWAC.

**Fig. 5(a)** shows the SEM micrographs of the GW and GWAC. It can be seen from the micrographs that the external surface of the GWAC is full of cavities compared with GW, and the pores were at different sizes and shapes. According to the micrograph, it seems that the cavities resulted from the evaporation of ZnCl\(_2\) during activation, leaving the space previously occupied by the ZnCl\(_2\). This micrograph indicates that it would be a good adsorbent in adsorption application from solution. This observation can be supported by textural characteristics of GWAC (Table 2).

**XRD technique** is a powerful tool to analyze crystalline nature of materials. **Fig. 5(b)** shows XRD profiles of the GW and GWAC. The XRD spectra of the dried GW indicated the amorphous structure of the raw material. However, the peak is wide and high. This indicates the existence of the crystalline units in the structure. As seen from the XRD spectra of the GWAC, after the activation process, the wide broad peak converted to two more narrow peaks as a result of the amorphous structure. In the XRD spectra of GWAC, two sharp peaks belong to trapped ZnO in its structure (Uvarov and Popov, 2007).
When comparing the two spectra, we can show the disappearance of many absorption bands in the carbon spectrum as a result of carbonization and activation process. This suggests the decomposition of these groups and subsequent release of their by-products as volatile matter by chemical activation at high temperature. In the spectra of GW, the bands at 3009 and 2853 cm⁻¹ are assigned to the aromatic and aliphatic C–H groups. The peak located at 1742 cm⁻¹ indicates the existence of esters in the structure. The peak located at 1581.86 cm⁻¹ related to C–C stretching vibrations and the band observed at 1167.21 cm⁻¹ corresponds to C–O–H stretching. In the FTIR spectra of GWAC, the peaks at the range of 1500–1000 cm⁻¹, correspond to carbonyl group, carboxylate ion, ash component and chelat bonded carboxylate structures (El-Hendawy, 2006; Lua and Yang, 2004).

According to the Boehm titration results (Table 2), GWAC exhibited a weak acidic property, with the surface acidity of 1.23 meq/g with the maximum composition of phenolic group (0.17 meq/g) with traces of lactonic (0.51 meq/g) and carboxylic (0.55 meq/g) groups, and 0.88 meq/g as surface basicity. pH in the water phase and pHpzc values of GWAC were determined as 5.86 and 6.20, respectively (Table 2). These values fall in the weak acidic region and shows that the weak acidic groups on the surface are dominant.

**Fig. 5(c)** shows the FT-IR spectra of the GW and GWAC.
This table, high R² calculated isotherm parameters are listed in Table 3. As seen from some commercial and vegetable-based ACs are listed in Table 4. Adsorption capacities of the GWAC with other reported values for 3.5. Comparison to some other carbonaceous materials.

A comparison of textural and adsorptive characteristics of GWAC and some commercial ACs listed in Table 4. Maximum monolayer adsorption capacities of 417 mg/g for MB and 386 mg/g for MY are obtained for both isotherm models as follows: 6:1 (w/w) ZnCl₂/GW. The GWAC which had the highest surface area and pore volume was obtained by these conditions as follows: 6:1 (w/w) ZnCl₂/GW. The GWAD could be employed as an efficient adsorbent for the removal of cationic and anionic dyes from wastewater.

3.6. Economic feasibility and cost-estimation

From the economic feasibility calculations made on our laboratory-scale production studies, the production yield was identified to be about 430 kg GWAC per ton of GW. According to our research from various sources via the internet, the cost of commercial AC in the world market varies between $700—5000 per ton based on the quality. The cost of AC production from GW from the calculations made on the three separate production studies was determined as about $200 per ton. Consequently, to produce AC from GW would be an economical selection for the commercial available AC.

4. Conclusion

Optimum conditions of AC production from GW were determined. The most important optimization parameter in the production was found to be the impregnation ratio of ZnCl₂/GW. The GWAC had the highest surface area and pore volume as obtained by these conditions as follows: 6:1 (w/w) ZnCl₂/GW. The GWAC had the highest surface area and pore volume was obtained by these conditions as follows: 6:1 (w/w) ZnCl₂/GW. The GWAC followed the Langmuir isotherm model, showing the maximum monolayer adsorption capacities of 417 mg/g for MB and 386 mg/g for MY. In conclusion, GWAC can be effectively used as a cleaner adsorbent material for the removal of cationic and anionic dyes from aqueous solution, in which its adsorption capacity is higher than many commercial and others agricultural waste-based carbonaceous adsorbents.

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References


