High surface area mesoporous activated carbon from tomato processing solid waste by zinc chloride activation: process optimization, characterization and dyes adsorption

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ABSTRACT

The aim of this study is to produce the activated carbon at optimum production conditions from the tomato processing waste by ZnCl2 activation. The influences of the production variables, such as impregnation ratio, carbonization temperature, and carbonization time on the some pore characteristics of produced carbons have been investigated, and the best production conditions were determined. The optimal activated carbon which had the highest surface area and pore volume was obtained by these conditions as follows: 6:1 impregnation ratio, 600 °C carbonization temperature and 1 h carbonization time. The optimum conditions resulted in an activated carbon with a carbon content of 53.92% and a yield of 38.20%, while the surface area of 1093 m2/g, with the total pore volume of 1.569 cm3/g, mesoporosity of 91.78% and average pore diameter of 5.92 nm. It was characterized by some physical and chemical techniques. Its adsorptive performance was tested using methylene blue and metanil yellow dyes. The adsorption behavior was well described by the Langmuir isotherm model, showing a maximum adsorption capacity for methylene blue and metanil yellow of 400 mg/g and 385 mg/g, respectively. The results revealed the potential use of optimal activated carbon for removal of cationic and anionic dyes.

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1. Introduction

Activated carbons (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 waste water treatment (Ceyhan et al., 2013). Their high surface areas and large pore volumes are caused by heterogeneous porous structures which make them perfect adsorbents. The demand for AC in the world due to these features is increasing day by day. The world demand for ACs was about 4.28 million metric tons in 2012, and it is expected to increase more than 10% per year over the next 5 years. This increased demand is mainly due to the more stringent pollution controls in the USA and China. For instance in China the existing plan, named the Twelfth Five-Year Plan (2011–2015), that seeks to improve the water and air quality through the use of more environmentally friendly processes will significantly increase the AC demand (Valente Nabais et al., 2013).

The ACs can be produced from a variety of natural and synthetic substances, lignocellulosic materials being one of the most used precursors. The composition of the lignocellulosic material regarding the cellulose, hemicellulose and lignin content determines, to some extent, the porosity development of the produced ACs (Valente Nabais et al., 2013). The production of ACs from agricultural by-products has received much attention from the scientific community as they are renewable, low-cost and environmentally friendly materials (Okman et al., 2014). In recent years, there has been increasing interest in the research on the production of ACs by using renewable and cheaper precursor. A large number of agricultural by-products, such as coffee grounds (Reflas et al., 2010), cocoa shell (Ahmad et al., 2012), waste tea (Auta and Hamed, 2011), coffee husks (Oliveira et al., 2009), pomegranate shell (Ghaedi et al., 2012), mahogany sawdust (Malik, 2003), rice husk (Malik, 2003; Santra et al., 2008), mehagani sawdust (Santra et al., 2008), coconut shell (Santra et al., 2008), bael shell, grape industrial processing waste (Saygili et al., 2015), etc. have been
2. Materials and methods

2.1. Materials

The precursor, TW was collected from a local tomato paste factory in Adana, Turkey. It was washed with water to take off impurities and subsequently dried naturally. Later, the solid waste was crushed and ground to pass through 80-mesh sieves prior to its chemical activation. ZnCl₂ of purity 99.9% was used as chemical activator in the AC production. The basic dye, MB (Type: cationic, chemical formula: C₂₃H₁₈N₃NaO₃S, Mw: 319.85 g/mol, color index: basic blue 9, λₘₐₓ: 665 nm) and acidic dye, MY (Type: anionic, chemical formula: C₁₆H₁₈ClN₃S, color index: acid yellow 36, λₘₐₓ: 433 nm, Mw: 375.38 g/mol) were used as sorbates. The used all chemicals were purchased from Sigma–Aldrich Company in Ankara, Turkey.

2.2. Optimization studies of production conditions

The optimal conditions for AC preparation from TW were determined by examining effects of the impregnation ratio (1:1, 2:1, 4:1, 6:1 and 8:1; ZnCl₂/TW, w/w), carbonization temperature (400, 500, 600 and 800 °C) and carbonization time (0.5, 1.0, 2.0 and 4 h). The experimental run of the production and conditions for ACs from TW are given in Table 1. These processes were performed by heating in a horizontal stainless-steel tubular reactor (7.0 cm diameter × 100 cm length). At every turn, twenty-five grams of the dry sample impregnated with ZnCl₂ was placed into the reactor and N₂ was passed through at a flow rate of 100 mL/min; the system was heated at a rate of 10 °C/min. The produced ACs were cooled down to room temperature under nitrogen flow, and 0.2 M HCl was added on to ACs. They 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. The yield of optimal AC was calculated as the ratio of the dry weight of produced AC to the weight of the air-dried of the precursor.

2.3. Characterization of tomato waste and its activated carbon

TW was characterized by thermogravimetry/differential thermogravimetry (TG/DTG) analysis, proximate, ultimate and biochemical component analysis, scanning electron microscopic (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopic (XPS) and Fourier transform infrared spectroscopic (FT-IR) while the optimal AC produced was characterized by proximate, ultimate, pore structure, SEM, XRD, XPS, FT-IR analysis, Boehm’s titration, pHbic and CEC. The thermal behavior of TW was measured with a thermogravimetric analyzer (Shimadzu, TG/DTA-50). About 10 mg of sample material was heated from 25 °C to 1000 °C at a ramping rate of 10 °C/min.

The experimental runs and conditions for ACs production, and pore characteristics [IR: Impregnation ratio; CT: Carbonization temperature; Ct: Carbonization time].

<table>
<thead>
<tr>
<th>Run</th>
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<th>Pore characteristics</th>
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<tr>
<td></td>
<td>IR (w/w) CT (°C) Ct (h)</td>
<td>S_{BET} (m²/g) V₁ (cm³/g) V_{mic} (cm³/g) V_{mic} (%) V_{max} (cm³/g) V_{max} (%) Dp (nm)</td>
</tr>
<tr>
<td>1</td>
<td>1:1</td>
<td>500 1.0 617 0.437 0.313 71 0.124 29 2.64</td>
</tr>
<tr>
<td>2</td>
<td>2:1</td>
<td>“ “ 722 0.457 0.304 66 0.153 34 4.49</td>
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<tr>
<td>3</td>
<td>4:1</td>
<td>“ “ 760 0.710 0.584 41 0.416 59 4.83</td>
</tr>
<tr>
<td>4</td>
<td>6:1</td>
<td>“ “ 787 1.000 0.277 28 0.723 72 5.78</td>
</tr>
<tr>
<td>5</td>
<td>8:1</td>
<td>“ “ 495 0.452 0.196 43 0.256 57 3.65</td>
</tr>
<tr>
<td>6</td>
<td>6:1</td>
<td>400 1.0 648 0.756 0.086 11 0.670 89 4.56</td>
</tr>
<tr>
<td>7</td>
<td>6:1</td>
<td>600 “ 1093 1.569 0.129 8 1.440 92 5.92</td>
</tr>
<tr>
<td>8</td>
<td>“ 6:1 800 “</td>
<td>“ 492 0.106 “ 0.058 55 0.048 45 2.41</td>
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<tr>
<td>9</td>
<td>6:1</td>
<td>600 0.5 522 0.662 0.191 29 0.471 71 5.02</td>
</tr>
<tr>
<td>10</td>
<td>“ 2.0 1034 1.451 0.440 30 1.011 70 5.61</td>
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<td>11</td>
<td>“ “ 400 1.0 617 0.437 0.313 71 0.124 29 2.64</td>
<td></td>
</tr>
</tbody>
</table>

Table 1

The experimental runs and conditions for ACs production, and pore characteristics [IR: Impregnation ratio; CT: Carbonization temperature; Ct: Carbonization time].
10 °C/min under nitrogen gas atmosphere with the low rate of 200 mL/min, and constantly weighed. Percent weight loss versus temperature plots were taken for the thermogravimetric (TG) analysis and the derivative weight loss against temperature was taken for the derivative thermogravimetric (DTG) analysis.

The advantage of the TW for AC production was first checked using various methods such as ultimate, proximate and biochemical component analysis. 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. Biochemical component analysis including extractives, lignin, hemi celluloses, and cellulose of TW 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.

Crystallographic characterization of TW and TAC were examined by XRD measurements performed on a Bruker D8 Discovery EVA diffractometer using monochromatic copper radiation (Cu Kα, λ = 0.1541 nm) at 40 kV and 40 mA over the 2θ range 0-80°. The surface physical morphologies of TW and TAC were identified by using SEM technique (jeol/jsm- 6335F, USA). The S BET, V T max, D p of the produced ACs were determined by using a surface area and pore size distribution analyzer (Micromeritics ASAP 2020). The V mic was determined by subtracting the V mic from the V T while the V mic(%) and V mes(%) were based on the V T.

In order to determine quantitatively and qualitatively surface functional groups of the optimal AC produced, FT-IR analysis and Boehm’s titration method (Boehm, 2002) were applied, respectively. 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. In addition, the surface properties of the TW and TAC were measured by XPS. These measurements were performed on THERMO K-ALPHA spectrometer with a monochromatic Al Kα source at 1486.7 eV, with a voltage of 15 kV and an emission current of 10 mA. The amounts of surface acidic and basic functional groups were determined by the Boehm’s titration method. This method is one of the most widely used methods to quantify acidic groups with different strengths on ACs. The various free acidic groups were determined using the assumption that NaOH neutralizes carboxyl, lactone and phenolic groups; Na₂CO₃ neutralizes carboxyl, lactone; NaHCO₃ neutralizes only carboxyl groups, respectively (Laszlo and Szucs, 2001). The total acidity and basicity were determined from the amount of NaOH and HCl, respectively. pHₐzc was determined using the pH drift method. The pHₐzc value is reflecting the combined influence of all the surface functional groups of samples. Net charge of the adsorbent under pHₐzc is positive, while it is negative above pHₐzc (Smiciklas et al., 2000). pH was measured in a distilled water suspension (12.5 mL) of 0.5 g of sample after heating at 90 °C and then cooling to room temperature (Reffas et al., 2010). CEC which is a scale to reversibly adsorb positively charged species of optimal AC was determined by the method described by Puziy et al. (2002).

2.4. Methylene blue and metanil yellow dye adsorption

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) of MB/MY-AC adsorption systems. The flasks were shaken mechanically at 120 rpm in a water bath shaker (Daihan- WSB-30) at 30 °C for 24 h, which is enough for guaranteeing adsorption equilibrium for both. After each adsorption process, the samples were filtrated for solid–liquid separation and the concentrations of MB and MY in the supernatant solutions were analyzed by a UV—vis spectrophotometer (Perkin Elmer-Lambda 25) at 665 and 433 nm of λ max, respectively. Each dye adsorption 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 for the equilibrium data obtained. The used linearized isotherm equations were:

Freundlich isotherm  \[ q_e = \ln K_F + \frac{1}{n_F} \ln C_e \]  (1)

Langmuir isotherm \[ \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m C_e} \]  (2)

The higher value of \( R^2 \) the more accurate is the model that predicts the experimental data.

Further, the \( S_{MB} \) and \( S_{MY} \) related to the MB and MY for pore characterization from aqueous phase were calculated from the following equation:

\[ S = \frac{10^{-20} M q_m d_p N_A}{M} \]  (3)

In this study, \( d_0 \) values taken for MB and MY dyes were 1.20 and 1.02 nm², respectively (Güzel, 1996).

3. Results and discussion

In this part, the properties of TW, the effect of conditions in the production of optimal AC and also the pore, surface and dyes adsorption property of the AC produced in optimal conditions were investigated.

3.1. Thermal analysis of the tomato waste

Thermal analysis has been widely used to get knowledge of the thermal behaviors of agricultural by-products. Thermograms obtained from the TG/DTG analysis of the TW as a function of temperature is shown in Fig. 1. As seen in this figure, the decomposition of TW takes place in four steps. The first step, which occurs at temperatures ranging from 28 to 150 °C, involves the loss of moisture present in the sample with approximately the weight loss of 4.45%. The second weight loss step with approximately the
weight loss of 5.25% was occurred at 150–280 °C. This step is related to the release of volatiles resulting from the decomposition of hemicellulose. In the third step the occurring at 280–480 °C is characterized with the decomposition of cellulose and lignin. The maximum rate of weight loss occurred at the third stage approximately with the weight loss of 52%. Nevertheless, in the fourth step (above 480 °C), no significant weight loss (0.95%) is observed. Therefore, this temperature can be said to be the lowest carbonization temperature for AC production from TW. In the DTG spectrum in Fig. 1, the endothermic peak around 98 °C, belongs to the removal of water. The weak endothermic peak around 470 °C belongs to hydroxyl deformation (Yang et al., 2007).

3.2. Selection of optimum process parameters

In order to produce optimal AC from the TW, the effects of experimental process variables represented by impregnation ratio (ZnCl₂/TW), carbonization temperature, and carbonization time on the pore characteristics such as S_BET, V_T, V_mes (%) and D_p determined from the nitrogen adsorption–desorption isotherms and pore size distribution graphs (Fig. 2a–c) of the ACs produced were demonstrated in Table 1. The obtained results are presented below under the sub-heads.

3.2.1. Effect of the impregnation ratio

Firstly, to see the effect of the chemical activation, TW was carbonized at 500 °C without ZnCl₂ activation. It had the BET surface area of 12.79 m²/g and V_T of 0.012 cm³/g. The effects of impregnation ratio (ZnCl₂/TW, w/w) on the S_BET, V_T, V_mes (%) and D_p of ACs produced for a carbonization temperature of 500 °C and carbonization time of 1 h are shown in Table 1. As seen in this table, while the impregnation ratio was increased from 1 to 6, the S_BET, V_T, V_mes (%) and D_p values of ACs produced increased from 617 to 787 m²/g, from 0.437 to 0.973 cm³/g, from 29% to 72% and from 2.64 to 5.78 nm, respectively, and above 6:1 these values decreased. From these results, it is understood that ZnCl₂ 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, preparing more micropores. But at higher impregnation ratio, the more swelling into impregnated precursor material and stronger release of volatiles in the carbonization process will lead to the widening of pores; micropores formed are subsequently converted to mesopores (Yang and Qiu, 2011). Consequently, the ratio of 6 was chosen as optimum impregnation ratio.

3.2.2. Effect of carbonization temperature

The production of ACs was carried out at different temperatures to be carbonized for the time of 1 h by keeping the impregnation ratio at 6:1. As seen from the Table 1, while temperature increased from 400 to 600 °C, the S_BET, V_T, V_mes (%) and D_p values increased from 648 to 1093 m²/g, from 0.756 to 1.569 cm³/g, from 89% to 92% and from 4.56 to 5.91 nm, respectively, and above 6:1 these values decreased. This increase is due to the formation of new pores by
continuation of the evaporating substances resulting from the decomposition of primary compounds of the TW with increasing of temperature. However, decrease in pore characteristics above 600 °C might be due to the sintering effect at high temperature, followed by shrinkage of the char, and realignment of the carbon structure which resulted in reduced pore areas as well as volume (Mohanty et al., 2006). Consequently, 600 °C was chosen as the optimum carbonization temperature for subsequent experiments.

3.2.3. Effect of carbonization time

The production of ACs was carried out at different carbonization time (0.5–4 h) to be activated for 600 °C by keeping the impregnation ratio at 6:1. As seen from the Table 1, while the time increased from 0.5 h to 1 h, the $S_{\text{BET}}$, $V_t$, $V_{\text{mes}}$(%) and $D_p$ values increased from 522 to 1093 m$^2$/g, from 0.662 to 1.569 cm$^3$/g, from 71% to 92% and from 5.02 to 5.92 nm, respectively. However, while the carbonization time increased from 1 h to 4 h, they were decreased. This decrease was possibly due to some of the pores being sealed off as a result of sintering for a prolonged time (Mohanty et al., 2006). Therefore, the time of 1 h min was chosen as the best carbonization time.

3.3. Process optimization

From the pore characteristics in Table 1, the optimal AC which had the highest $S_{\text{BET}}$, ($1063$ m$^2$/g), $V_t$, $V_{\text{mes}}$(%) and $D_p$ values increased from 522 to 1093 m$^2$/g, from 0.662 to 1.569 cm$^3$/g, from 71% to 92% and from 5.02 to 5.92 nm, respectively. However, while the carbonization time increased from 1 h to 4 h, they were decreased. This decrease was possibly due to some of the pores being sealed off as a result of sintering for a prolonged time (Mohanty et al., 2006). Therefore, the time of 1 h min was chosen as the best carbonization time.

3.4. Characterization

3.4.1. Proximate, elemental and biochemical component analysis

The proximate, ultimate and component analysis results revealed that TW contains 56.96% holocellulose (33.17% cellulose + 23.79% hemicellulose), 35.70% lignin, 7.34% extractives, 2.95% moisture, 82.67% volatile matter, 12.80% fixed carbon, 1.58%ash, 58.95% carbon, 8.21% hydrogen, 0.12% sulfur and 29.77% oxygen as expected for most lignocellulosic material. The high carbon, low ash and low sulfur content of the precursor are positive factors and therefore, these wastes can be potential precursor materials for the production of AC (Stavropoulos and Zabaniotou, 2005; Açıkýl Todd et al., 2014). Although TW has very high volatile content, low ash content and a reasonable amount of carbon makes it a suitable precursor for the carbon sorbent production having large porous.

The proximate and ultimate analysis results related to the TAC are given in Table 2. It can be seen that the contents of carbon and ash increased, in the TAC according to the TW, whereas the contents of hydrogen, nitrogen, oxygen and sulfur decreased. This is due to the release of volatiles during carbonization, which can result in the elimination of the non-carbon compounds (Chen et al., 2013). The TAC also possessed a low content of ash (25.56%) indicating a high-quality carbon sorbent. Low ash content typically leads to superior removal of organic substances from aqueous phase due to the hydrophobicity of the material (Zuim et al., 2011).

3.4.2. Pore analysis

The nitrogen adsorption—desorption isotherms (inset) as well as the pore size distributions for the TAC are shown in Fig. 2c. The shape of its N$_2$ adsorption—desorption isotherm was a mixture of types I and IV in BDDT (Brunauer, Deming, Deming and Teller) classification, as defined by the IUPAC (Sing et al., 1985), with a wider hysteresis loop (H4) at high relative pressures, suggesting that it had a mixed microporous and mesoporous structure (Wang et al., 2012). The main pore characteristics of TAC obtained from the nitrogen adsorption—desorption isotherms were summarized in Table 2, indicating that it has a large $S_{\text{BET}}$ $(1093$ m$^2$/g) and $V_t$ $(1.569$ cm$^3$/g). Pore size distribution is a very important property of porous sorbents because the difference in the pore size affects the adsorption capacity for molecules of different sizes and shapes, and also this is one of the criteria by which carbon sorbents are selected for a particular application. According to the classification adopted by IUPAC, sorbent pores are classified into three groups: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm) (Xiao et al., 2012). Fig. 2c presents the pore size distribution for the TAC. As seen this figure, the dominant pore of TAC is in the range of 4–95 nm, and its average pore diameter is 5.92 nm. Therefore, it is typically a mesoporous carbon sorbent. This can also be concluded from the results in Table 2, which show a $V_{\text{mes}}$ of 1.440 cm$^3$/g compared to a $V_{\text{mic}}$ of 0.129 cm$^3$/g. These results indicate that a significant amount of $V_{\text{mic}}$(%) (91.78%) and a certain amount of $V_{\text{mes}}$(%) (8.22%) were formed in the TAC. These results indicate that TW is efficient precursor for production of mesoporous AC having high surface area and large pore volume. Table 3 shows a comparison of the $S_{\text{BET}}$ of the TAC with other reported values for agrwaste-based ACs in literatures.

### Table 2

<table>
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<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
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<td>$V_t$(cm$^3$/g)</td>
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<td>$V_{\text{mes}}$(cm$^3$/g)</td>
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<td>$V_{\text{mic}}$(cm$^3$/g)</td>
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<td>$V_{\text{mes}}$(%)</td>
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<td>$D_p$(nm)</td>
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</table>

*$^*$ By difference.

3.4.3. SEM analysis

Fig. 3(a) and (b) show the SEM micrographs of the TW and TAC, respectively. Moreover, TAC has some cavities, not full of cavities. The cavities are caused by chemical activation with ZnCl$_2$ during carbonization. Namely, ZnCl$_2$ catalyzes the polymerization reactions (Scholl condensation reactions) between tar-forming compounds and aromatic hydrocarbons in the structure of precursor (Ahmadpour and Do, 1997). The polycyclic compounds with aromatic hydrocarbons in the structure of precursor are typically a mesoporous carbon sorbent. This can be also concluded from the results in Table 2, which show a $V_{\text{mes}}$ of 1.440 cm$^3$/g compared to a $V_{\text{mic}}$ of 0.129 cm$^3$/g. These results indicate that a significant amount of $V_{\text{mic}}$(%) (91.78%) and a certain amount of $V_{\text{mes}}$(%) (8.22%) were formed in the TAC. These results indicate that TW is efficient precursor for production of mesoporous AC having high surface area and large pore volume. Table 3 shows a comparison of the $S_{\text{BET}}$ of the TAC with other reported values for agrwaste-based ACs in literatures.

3.4.4. XRD analysis

Fig. 4 shows the XRD patterns of the TW and TAC. In the TW, a broad peak appearing at 2θ = 21.8° was attributed to the
characteristic crystal structure of cellulose \cite{Regmi2012}. The intensity of the peak largely decreased after carbonization due to the decomposition of the cellulose. Two broad peaks appeared at approximately $2\theta = 25^\circ$ and $43^\circ$ after activation with ZnCl$_2$ in TAC. They corresponded to the formation of hexagonal graphite structures (0 0 2) and (1 0 0) (overlapped 1 0 0 and 1 0 1). In addition, the

\begin{table}[h]
\centering
\caption{BET surface area comparison of TAC with other agricultural waste-based ACs reported in literatures \cite{IR: Impregnation ratio; CT: Carbonization temperature; Ct: Carbonization time}.}
\begin{tabular}{|l|c|c|c|c|c|c|}
\hline
Precursor & Atmosphere & Activating agents & IR (w/w) & CT (\degree C) & Ct (h) & $S_{BET}$ (m$^2$/g) & References \\
\hline
Grape stalk & CO$_2$ & ZnCl$_2$ & 2.0 & 700 & 2.0 & 1411 & Ozdemir et al., 2014 \\
Pistachio nutshell & N$_2$ & ZnCl$_2$ & 1.0 & 400 & 1.0 & 1635 & Lua and Yang, 2005 \\
Coffee husk & N$_2$ & ZnCl$_2$ & 1.0 & 550 & 3.0 & 1522 & Oliveira et al., 2009 \\
Waste potato residue & N$_2$ & ZnCl$_2$ & 1.5 & 600 & 1.0 & 1357 & Zhang et al., 2015 \\
Fox nutshell & N$_2$ & ZnCl$_2$ & 2.0 & 800 & 1.0 & 2869 & Kumar and Jena, 2015 \\
Grape waste & N$_2$ & ZnCl$_2$ & 6.0 & 600 & 1.0 & 1455 & Saygılı et al., 2015 \\
Coffee husks & N$_2$ & FeCl$_3$ & 1.0 & 280 & 1.0 & 965 & Oliveira et al., 2009 \\
Spartina alterniflora & N$_2$ & KOH & 3.0 & 450 & 1.5 & 2825 & Liu et al., 2013 \\
Plum kernels & N$_2$ & NaOH & 4.0 & 780 & 1.0 & 1887 & Tseng, 2007 \\
Corn cob & N$_2$ & H$_3$PO$_4$ & 1.0 & 400 & 1.0 & 2081 & Sych et al., 2012 \\
Rice straw & Air & (NH$_4$)$_2$HPO$_4$ & 5.0 & 200 & 2.0 & 1154 & Gao et al., 2011 \\
Sunflower oil cake & N$_2$ & H$_2$SO$_4$ & 0.85 & 600 & -- & 240 & Karagoz et al., 2008 \\
Waste tea & N$_2$ & CH$_3$COO & 1.4 & 800 & 2.0 & 854 & Auta and Hameed, 2011 \\
Tomato waste & N$_2$ & ZnCl$_2$ & 6.0 & 600 & 1.0 & 1093 & This study \\
\hline
\end{tabular}
\caption*{Fig. 3. SEM micrographs of TW and TAC.}
\caption*{Fig. 4. XRD spectra of TW and TAC.}
XRD pattern of TAC contains sharp peak at 2θ = 35.3° which was due to the presence of zinc oxide and zinc carbides on the washed TAC surface. The sharpness of the peak indicates that the zinc presented is comparatively large, though still in the micro range (Danish et al., 2013).

3.4.5. FT-IR analysis

The FT-IR spectra of TW and TAC are shown in Fig. 5. The spectra exhibit a number of absorption peaks, indicating the complex nature of the materials. In the spectra of TW in Fig. 5, the presence of the broad and intense absorption peak at 3323.17 cm\(^{-1}\) indicates the O–H stretching vibrations of cellulose, pectin, absorbed water, hemicellulose, and lignin (Gündogdu et al., 2013). The peak observed at 3003.96 cm\(^{-1}\) can be attributed to the aliphatic saturated C–H stretching vibrations of in lignin polysaccharides including cellulose and hemicellulose. The two notable bands observed at 2923 cm\(^{-1}\) and 2853 cm\(^{-1}\) due to the symmetric and asymmetric stretching vibration of methyl groups (Gündogdu et al., 2013; Nguyen et al., 2013). The presence of the peak at 1743.27 cm\(^{-1}\) indicates the carbonyl (C=O) stretching vibration of the carboxyl groups of pectin, hemicellulose and lignin (Njoku et al., 2013; Hameed and Daud, 2008). The peak at 1635.10 cm\(^{-1}\) corresponds to absorbed water H–O–H bend. The vibrations at 1453.96 cm\(^{-1}\) and 1375.75 cm\(^{-1}\) could be due to aliphatic and aromatic (C–H) groups in the plane deformation vibrations of methyl, methylene and methoxy groups (Hameed and Daud, 2008; Huang et al., 2015; Angin, 2013). The bands in the range of 1250–1000 cm\(^{-1}\) can be assigned to the C–O stretching vibration of carboxylic acids and alcohols. The band at 721.64 cm\(^{-1}\) is related to aromatic, out of plane C–H bending with different degrees of substitution (Angin, 2013; Mastalerz and Bustin, 1995). After carbonization, the FT-IR spectrum of TAC was markedly different from TW. The broad band located in the region of 3100–3400 cm\(^{-1}\) related to O–H stretching vibrations existed but shifted to the high wavenumber. The band located at about 1581.71 cm\(^{-1}\), which could be attributed to (C=O) vibration in aromatic rings (Lua and Yang, 2005; Li et al., 2015). The band at 1228.21 cm\(^{-1}\) is due to the C–O stretching vibration of phenol group (Hameed and Daud, 2008; Angin, 2013). The many absorption bands disappeared when the FT-IR spectrum for the TAC are compared to that for TW. This is likely to be due to the vaporization of organic matter at high temperatures.

3.4.6. XPS analysis

In order to further investigate the surface chemistry composition of the materials, XPS analysis was performed for the prior and after carbonization. Fig. 6 shows the XPS spectra of TW and TAC. For the TW (Fig. 6a), the high resolution C1s spectrum can be fitted to three components corresponding to the C=C (284.37 eV), C–O–C (285.9 eV) and –COOR (288 eV) with the relative percentages of 41.75%, 30.25% and 5.98%. After carbonization, the C1s spectrum of TAC (Fig. 6c) was resolved into two individual component peaks: the groups of C=C (284.68 eV) and the groups of C–O–C (285.91 eV). No carboxylic acid and/or ester groups (–COOR) are detected. The absence of –COOR groups could be attributed to a decrease in C–O–C (17.21%) groups and a decrease in C–O–C (72.83%) and a decrease in C–O–C (30.25%) groups. This means that the pyrolysis tends to increase the carbon fraction mainly due to the volatilization of the oxygenated compounds (Ncibi et al., 2009). On the other hand, Fig. 6b shows that the O1s region in the XPS spectrum of TW exhibits two deconvoluted peaks at 530.75 and 532.24 eV, representing carboxylic acid and/or ester groups (O=C=O) and oxygen singly bonded to carbon in phenols and ethers groups (C–O), respectively. Fig. 6d shows the typical high resolution XPS spectra of the O1s region of TAC. As can be seen from this figure, O1s XPS spectrum of TAC was fitted to two components: (I) metal oxides (531.11 eV) and (II) oxygen singly bonded to carbon in phenols and ethers groups (C–O), respectively. The XPS analysis results indicate that significant differences existed on the percentage amounts of carbon and oxygen fractions after carbonization procedure, which is in agreement with the above FT-IR and Boehm's titration results.

3.4.7. Quantitative surface analysis

According to the Boehm titration results in the Table 2, it exhibited a weak acidic property, with the surface acidity of
1.16 meq/g with the maximum composition of phenolic group (0.13 meq/g) with traces of lactonic (0.51 meq/g) and carboxylic (0.52 meq/g) groups, and 1.04 meq/g as surface basicity. The concentration of lactonic and carboxyl groups was significantly higher compared with the phenolic group, indicating that carboxyl group was more prevalent on the surface. Furthermore, the surface of the TAC has substantially equal concentration of the basic and acidic group referring to an adsorptive, which is effective in the removal of anionic and cationic dyestuffs. The pH and pHpzc values for the TAC were found to be 5.80 and 6.17, respectively. The pH value falls in the slightly acidic region and value of pHpzc < 7 shows dominant of acidic groups over basic groups.

3.4.8. Methylene blue and metanil yellow adsorption analysis

Fig. 7 shows equilibrium isotherms of MB and MY at 30 °C onto TAC. The experimental equilibrium data in this figure are fitted with Freundlich and Langmuir linear isotherm equations (Eqs. (1)–(2)). The isotherm constants related to these models were obtained according to the intercept and slope from the plots between lnqe vs. lnCe and Ce/qe vs. Ce (not shown). Isotherm parameters and R² values obtained from the two isotherm models are summarized in Table 3. As seen from this table, R² values obtained for both isotherm models revealed that the equilibrium data for both dyes fitted well to the Langmuir isotherm under the studied conditions. The maximum sorption capacities (qm) calculated by the Langmuir equation of the MB and MY onto TAC are 400 and 385 mg/g, respectively (Table 4). A comparison of the pore characteristics and maximum sorption capacities of the TAC with other reported values for some commercial and vegetable-based ACs are listed in Table 5. The results in this table showed that the TAC can be effectively used for the removal of cationic and anionic dyes from aqueous solution, in which its sorption capacity is higher than many commercial and others agricultural waste-based carbonaceous sorbents. Furthermore, a value for 1/nF for both dyes was found to range between zero and one, indicating that the sorption condition was favorable. Besides, the 1/nF values obtained for MB sorption were lower in comparison to MY sorption, leading to conclusion that TAC is more efficient sorbent for the removal of cationic dye than anionic dye.

Table 4

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kF (mg/g) (L/mg)¹/n</td>
<td>1/n</td>
</tr>
<tr>
<td>MB</td>
<td>65</td>
<td>0.259</td>
</tr>
<tr>
<td>MY</td>
<td>47</td>
<td>0.301</td>
</tr>
</tbody>
</table>
4. Conclusion

The influence of operating parameters on the pore properties of the produced carbons followed a sequence of carbonization temperature > carbonization time > impregnation ratio. The optimal AC produced by chemical activation with ZnCl₂ attained maximum value of $S_{\text{BET}}$ as 1093 m²/g, a $D_p$ as 5.92 nm and a $D_{\text{mic}}$ as 6.17 at carbonization temperature of 600 °C for 1 h with an impregnation ratio of 6. These results showed that the TW seemed to be an alternative precursor for the commercial AC production. The equilibrium data of both dye adsorptions onto TAC followed the Langmuir isotherm model, showing the maximum monolayer adsorption capacities of 400 mg/g for MB and 385 mg/g for MY. Consequently, TAC can be used as a cleaner sorbent for solving many current-day environmental pollution problems and other applications.

Acknowledgments

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List of abbreviations

- $d_{\text{B}}$: Cross section area of one molecule of dye (nm²)
- $b$: Langmuir equilibrium constant related to the energy of sorption (L/mg)
- $C_0$: Initial concentration of dye (mg/L)
- $C_e$: Equilibrium concentration of dye (mg/L)
- $C_{\text{EC}}$: Cation exchange capacity (meq/g)
- $D_p$: Average pore diameter (nm)
- $K_F$: Freundlich constant representing adsorption capacity ($mg/g$) ($L/mg$ )
- $m$: Molecular weight of dye (g/mole)
- $n_F$: Adsorption intensity
- $pH_{ZC}$: pH at the point of zero charge of surface
- $q_m$: Maximum adsorption capacity of sorbate per unit mass of sorbent (mg/g)
- $q_{m,\text{MB}}$: Maximum adsorption capacity for Methylene Blue (mg/g)
- $q_{m,\text{MY}}$: Maximum adsorption capacity for Metanil Yellow (mg/g)
- $R^2$: Correlation coefficient
- $S_{\text{BET}}$: BET (Brunauer-Emmett-Teller) surface area (m²/g)

Table 5

<table>
<thead>
<tr>
<th>ACs</th>
<th>$q_{m,\text{MB}}$ (mg/g)</th>
<th>References</th>
<th>ACs</th>
<th>$q_{m,\text{MY}}$ (mg/g)</th>
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<tr>
<td>Filtrasorb-300</td>
<td>240</td>
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<td>Pomegranate</td>
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<td>Ghaedi et al., 2012</td>
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<td>455</td>
<td>Qada et al., 2013</td>
<td>Mahogany sawdust</td>
<td>184</td>
<td>Malik, 2003</td>
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<tr>
<td>Coffee grounds</td>
<td>182</td>
<td>Refias et al., 2010</td>
<td>Rice husk</td>
<td>87</td>
<td>Malik, 2003</td>
</tr>
<tr>
<td>Cocoa shell</td>
<td>213</td>
<td>Ahmad et al., 2012</td>
<td>Mehagani sawdust</td>
<td>118</td>
<td>Santra et al., 2008</td>
</tr>
<tr>
<td>Waste tea</td>
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<td>Aata and Hameed, 2011</td>
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<td>Santra et al., 2008</td>
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<td>Santra et al., 2008</td>
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<tr>
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<td>Sayghi et al., 2015</td>
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<td>386</td>
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<tr>
<td>Tomato waste</td>
<td>400</td>
<td>This study</td>
<td>Tomato waste</td>
<td>385</td>
<td>This study</td>
</tr>
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</table>

Otherwise, by evaluating in the Eq. (3) of maximum adsorption capacity values obtained from the Langmuir linear equation, the surface area values ($S_{\text{MB}}$ and $S_{\text{MY}}$) according to the MB and MY dyes were calculated as 903 and 630 m²/g, respectively. Furthermore, by taking $N_2$ as basis, the percent portions ($S_{\text{MB}}/S_{N_2}$ and $S_{\text{MY}}/S_{N_2}$) of the MB and MY for the reaching to the surface relative to N₂ were determined as 83 and 58%, respectively. These results also confirm that TAC has a mesosporous pore structure and a perfect adsorptive selectivity for anionic and cationic dyes removal from aqueous phase.

References


