SYNTHESIS OF ACTIVATED CARBON IN THE PRESENCE OF HYDROCHAR FROM CHICKPEA STALK AND ITS CHARACTERIZATION

N. GENLI[a], Ö. ŞAHIN[b], O. BAYTAR[b], S. HOROZ[c,*]
[a]*Dicle University, Diyarbakir Vocational School Of Technical Sciences, Chemical and Chemical Processing Technologies, Diyarbakır,, Turkey, 21280*
[b]*Siirt University, Engineering Faculty, Department of Chemical Engineering, Siirt, Turkey, 56100*
[c]*Siirt University, Engineering Faculty, Department of Electrical and Electronics, Siirt, Turkey, 56100*

In this study, hydrochar was obtained from chickpea stalk by hydrothermal method. Then, activated carbon was synthesized by chemical activation method using $ZnCl_2$ activator in the presence of this hydrochar. The effects of parameters such as impragnation rate (hydrochar/$ZnCl_2$), impragnation rate, activation temperature and activation time on activated carbon synthesis were investigated. The iodine number of the obtained activated carbon was determined and its characterization was performed by SEM, BET, FTIR measurements. It was determined that the highest iodine number of synthesized activated carbon was 734 mg/g under conditions of impragnation time (24 hour), impragnation rate (1/2), activation temperature (400 ^oC), and activation time (45 minutes). The BET surface area of the activated carbon with the highest iodine number was determined as 572 m^2/g. The methylene blue number of synthesized activated carbon and hydrochar were found as 105 mg/g and 45 mg/g, respectively.

(Received December 2, 2020; Accepted March 9, 2021)

Keywords: Activated carbon, Characterization, Hydrochar idoine number, Synthesis

1. Introduction

Activated carbon, also called activated charcoal, is basically defined as a porous solid material with black carbon with high specific surface area, proper pore size distribution and high surface reactivity [1]. Activated carbon is an amorphous and non-graphitic microcrystalline with a turbostractic structure. The size and thickness of each microcrystal is approximately 1–3 nm and 1–1.3 nm, respectively [2-4].

The synthesis of activated carbon consists of two basic procedures: carbonization and activation [5]. The purpose of carbonization is to reduce the volatile content of raw materials through pyrolysis of carbon precursors and to create a primary porous structure associated with high fixed carbon content. The purpose of activation is to improve the specific surface area or pore volume of activated carbon by opening new pores and enhancing existing pores. Apart from that, the activation can change or adjust the surface chemical structure of activated carbon with certain unique properties [6-7]. Activation is more important than carbonization in terms of the properties of activated carbon. Therefore, more emphasis is placed on activation [8-9]. Three main activation techniques are currently used to produce activated carbon: physical activation, chemical activation and physiochemical. Physical activation is a two-stage process involving the carbonization stage in the presence of an inert gas (N_2 or Ar) followed by the activation stage with the help of an oxidizing gas (O_2, CO_2, H_2O vapor) in the temperature range of 800-1200 °C [10]. Chemical activation, known as "wet oxidation", is a one-step process in which carbonization and activation occur simultaneously in the temperature range 450-850 °C [11]. The advantages of chemical activation are low heating temperature, short processing time, high carbon yield, well controlled porosity and high specific surface area. Physicochemical activation is a combination of physical

* Corresponding author: sabithoroz@siirt.edu.tr

and chemical processes involving the physical activation step under an oxidizing gas atmosphere followed by chemical impregnation of carbon precursors with activating agents [12].

Hydrothermal carbonization is an innovative method of thermal conversion of wet biomass at moderate temperature and autogenous pressure [13]. It consists of converting organic raw material into bio-oil, gas and a carbon-rich solid product in the presence of water. Their yield and physico-chemical properties are related to the raw material structure and operating conditions [14].

The cultivation area of the chickpea plant in the world is 17.815.000 hectares, its production is 17.192.000 tons and its yield is 970 kilograms/hectare. In our country, 514,416 hectares of cultivation area, 630,000 tons of production and 1,230 kilograms/hectare yield are obtained. The main reason why chickpea plant is produced in such a wide area is that it can be grown successfully in marginal areas, it does not need much nitrogen fertilizer and leaves a clean and productive area for the plant that will come after it [15].

In this study, activated carbon production parameters were determined by chemical activation method using $ZnCl_2$ activator in the presence of hydrochar obtained from chickpea stalk. The iodine adsorption and methylene blue number of the obtained activated carbons were determined.

2. Materials and Methods

2.1. Materials

All chemicals used in experimental studies were obtained from Merck and they are of analytical grade. Chickpea stalk from the market town of Siirt (Turkey) were obtained. Distilled water was used in the experiments.

2.2. Hydrothermal Carbonization

Hydrothermal carbonization was carried out in a 100 ml stainless steel autoclave with 3 g of ground chickpea stalks and 60 ml of distilled water. The autoclave was heated to 200 °C, then left for 5 hours and then cooled to ambient temperature. Reaction temperature (200 °C) and time (5 hours) were determined based on high yield according to the literature [16]. The solid product, called the chickpea stalk hydrochar, was separated by filtration and washed several times with distilled water. The obtained chickpea stalk hydrochar was preserved for use in

2.3. Preparation of Activated Carbon

Activated carbon was synthesized by chemical activation method in the presence of chickpea stalk hydrochar using $ZnCl_2$ activator. Synthesis of activated carbon; 3g of chickpea stalk hydrochar dissolved in 10 ml of distilled water was mixed with 3g of $ZnCl_2$ activator and left at room temperature for 24 hours. Chemical impregnated chickpea stalk hydrochar samples were prepared in the presence of N_2 at 500 ^oC activation temperature for 45 minutes. Activated carbon was synthesized by subjecting it to the activation period. The synthesized activated carbon was washed with 0.5 M HCl and then washed with hot distilled water until the pH value was 6-7. Effects of impragnation rate, impragnation time, activation temperature and activation time on activated carbon synthesis were investigated.

2.4. Characterization of Activated Carbon

The iodine number of the obtained activated carbon was determined. Iodine adsorption is performed to learn more about the porous structure of activated carbon. Iodine adsorption in liquid phase is considered a simple and rapid test. The surface area of the pores with a radius greater than 1 nm is determined by the iodine number. The iodine number is considered to be a basic parameter used to characterize activated carbon performance [6]. The method used by the American test and material community was used in determining the iodine number. The iodine number was calculated using Equation 1.

$$iodine\ number\ = \frac{(B-A)x127xNx40}{mxB} \quad (1)$$

A: The amount of $Na_2S_2O_3.5H_2O$ spent in the titration process after iodine adsorption of activated carbon (mL)
B: The amount of $Na_2S_2O_3.5H_2O$ spent in the titration process for 0.1 N iodine solution (mL)
N: Iodine solution concentration (N)
m: Amount of activated carbon (g)

The BET surface area of activated carbon with high iodine number was determined with the Quantachrome Nova 1200 series device. The characterization of the activated carbon with the highest surface area was carried out with SEM and FTIR devices and the methylene blue number was determined. The methylene blue number is calculated by Equation 2.

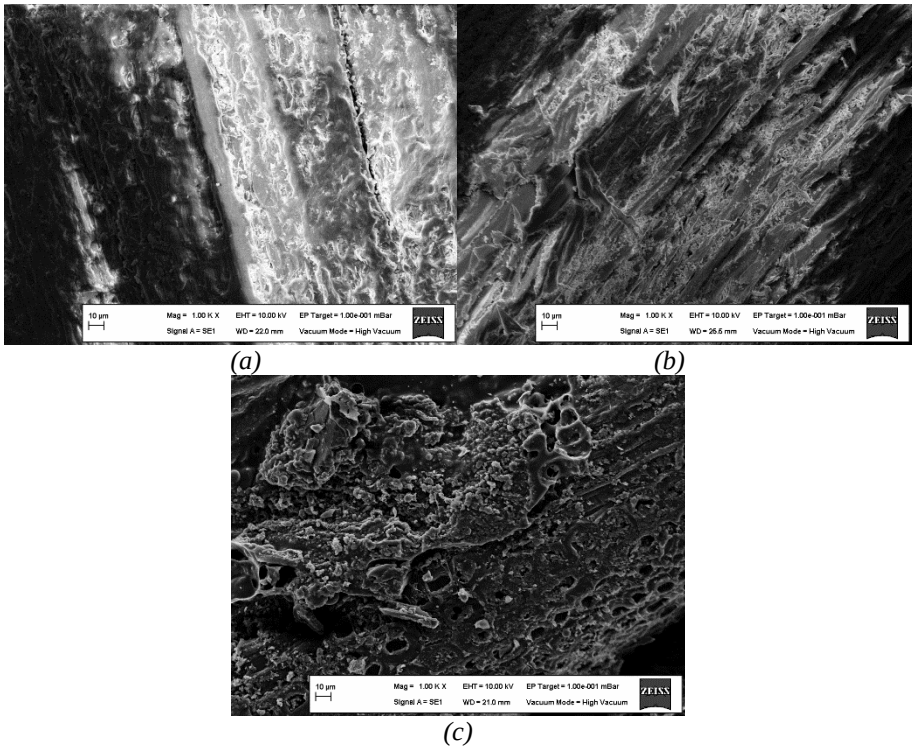
$$q_e = \frac{(C_0-C_e)}{w}V \quad (2)$$

q_e : The amount of substance adsorbed per unit adsorbent (mg/g)
C_o : Initial concentration of Solution (mg/L)
C_e : Concentration of the substance not adsorbed in solution at equilibrium (mg/L)
V : Solution volume (mL)
w : Amount of adsorbent (g)

3. Results and discussion

3.1. Activated carbon characterization

SEM images of chickpea stalk, hydrochar and activated carbon are given in Figure 1 (a-c).



(a) *(b)*

(c)

Fig. 1. SEM images; a-) Chickpea Stalk, b-) Hydrochar, c-) Activated carbon.

It can be seen from Figure 1a that the chickpea stalk has no pores on its surface and its surface is rough. Figure 1b reveals that the surface of the chickpea stalk becomes more rough by

subjecting it to hydrothermal treatment and it is not porous. It can be seen from Figure 1c that the surface of activated carbon synthesized with $ZnCI_2$ activator is porous. It has been observed that the synthesized activated carbon is porous and has more micro pores. The pores of activated carbon appear to be irregular and heterogeneous. SEM images of activated carbon obtained by using ZnCI2 activator in the presence of watermelon peel; It was stated that it has an irregular and heterogeneous surface morphology with a well-developed porous structure of various sizes [17].

The surface area and pore distributions of the synthesized activated carbon are given in Table 1.

Table 1. Surface area and pore distribution of activated carbon.

Surface Area (m^2/g)	Total Pore Volume (cc/g)	Micropore Surface Area (m^2/g)	Average Pore Diameter Distribution (nm)
572	9,189	352	32,1

It is seen from Table 1 that the surface area of the activated carbon synthesized is 572 m^2/g. 61% of the surface area of activated carbon consists of micropores. The average pore diameter distribution also supports this result.

Figure 2 gives information about FTIR analysis results of chickpea stalk, hydrochar and activated carbon.

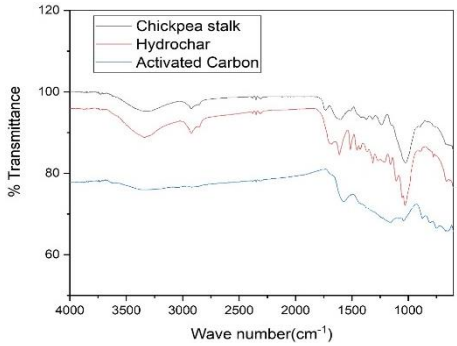


Fig. 2. Results of FT-IR analysis.

It is striking that there are more than one functional group in the chickpea stalk structure. The peak of 3300 cm^{-1} wave number indicated the presence of OH^- functional group connected by hydrogen bonds. The C-H functional group belonging to the methyl groups was observed at 2900 cm^{-1}, while the C=O functional group originating from the esters showed the presence of 1750 cm^{-1}. Peaks at 1250 and 1050 cm^{-1} indicate the presence of the C-O bond and the C-OH functional group, respectively. Although most of the functional groups in the chickpea stalk structure are also found in the hydrochar, some functional groups were observed. The structures that are not found in chickpea stem are the C=C functional group (1560 cm^{-1}) caused by the bond vibration and the C-O functional group (1260-1000 cm^{-1}) originating from phenols, respectively. It wasd determined that while activated carbon has the same functional groups in the structure of chickpea stem and hydrochar, some functional groups disappear.

The methylene blue number of synthesized activated carbon and hydrochar were determined to be 105 mg/g and 45 mg/g, respectively. The high number of methylene blue is an indication that its active structure is meso and microporous [8]. As can be seen from the SEM image and the BET surface area, the meso and microporous structure of activated carbon supports this result.

Since the impragnation rate has a very important place in activated carbon production, the effect of the impragnation rate was examined first.

The effect of impragnation rate (hydrochar / $ZnCl_2$) on the synthesis of activated carbon obtained from hydrochar was investigated in the presence of impragnation time (24 hours), activation temperature (500 ^oC) and activation time (45 min.). Variation of impragnation rate with iodine number is given in Figure 3.

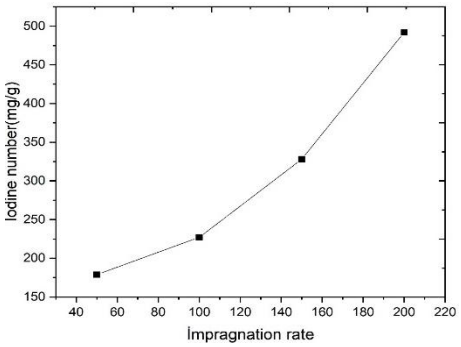


Fig. 3. Variation of impragnation rate with iodine number.

As seen in Figure 3, the impragnation rate causes an increase in the iodine number. While the impragnation rate was 50%, the iodine number was 179 mg/g and the impragnation rate was 200%, while the iodine number was 492 mg/g. It is thought that with the increase of impragnation rate, $ZnCl_2$ activator in the environment causes an increase in micropores. Teimouri et al. stated that the iodine number of the activated carbon, which they obtained from walnut shell using $ZnCl_2$ activator, increased with the increasing number of impragnation. They reported that the probable cause of this situation could be explained by the greater number of adsorption sites for iodine molecules made available at the higher impregnation rate [18].

After determining the impragnation rate, another parameter affecting activated carbon synthesis, the effect of activation temperature, was observed. The effect of activation temperature was investigated in the presence of impragnation time (24 hours), impragnation rate (200%) and activation time (45 min.). Variation of activation temperature with iodine number is given in Figure 4.

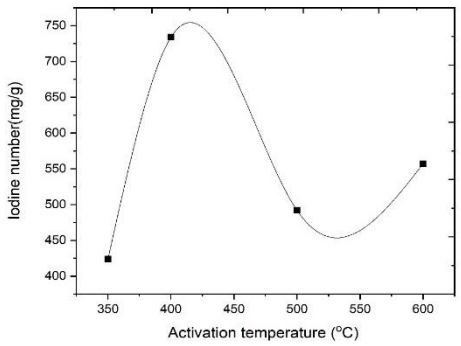


Fig. 4. Variation of activation temperature with iodine number.

When the activation temperature increased from 350 ^oC to 400 ^oC, the iodine number increased, while when the activation temperature was 500 ^oC and above, the iodine number decreased. Iodine numbers at different activation temperatures are given in Table 2.

Table 2. Iodine numbers at different activation temperatures for activated carbon.

Activation temperature (^{0}C)	Iodine numbers (mg/g)
350	424
400	734
500	492

It is considered that at low activation temperatures, there is not enough temperature for the activated carbon pores to open completely. When the activation temperature is 500 ^{o}C and above, it is thought that the pores of the activated carbon collapse due to the high temperature. Akçakal et al. investigated the effect of activation temperature on activated carbon synthesis by using ZnCl2 activator in the presence of a hard shell agricultural waste mixture. They stated that the surface area increases with increasing activation temperature and this is due to the catalytic effect of $ZnCl_2$ on pyrolytic decomposition [19].

Another parameter that affects activated carbon synthesis is the activation time. The effect of activation time was studied in the presence of impragnation time (24 hours), impragnation rate (200%) and activation temperature (400 ^{o}C) conditions. Variation of activation time with iodine number is given in Figure 5.

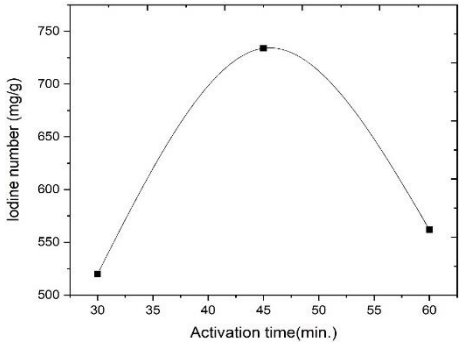


Fig. 5. Variation of activation time with iodine number.

It was observed that when the activation time increased from 30 min. to 45 min., the iodine number increased and then decreased. It is thought that when the activation time is 30 min., the pores are not opened sufficiently and when the activation time is 60, the micro pores turn into mesopores. Shoaib et al. studied the effect of activation time parameter on activated carbon synthesis using $ZnCl_2$ activator in the presence of sea lettuce. They stated that with increasing activation time, more gases are removed from the active carbon structure and this causes mesopore formation on the activated carbon surface [20].

In the present study, the effect of impragnation time on activated carbon synthesis is also discussed. Impragnation time effect was investigated in the presence of impragnation rate (200%), activation time (45 min.) And activation temperature (400 ^{o}C) conditions. Variation of impragnation time with iodine number is given in Figure 6.

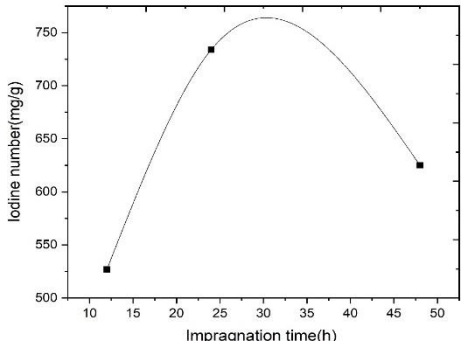


Fig. 6. Variation of impragnation time with iodine number.

The number of iodine obtained at different impragnation times is given in Table 3.

Table 3. The number of iodine obtained at different impragnation times for activated carbon.

Impragnation time (min.)	Iodine numbers (mg/g)
12	527
24	734
48	625

The reasons for observing different iodine numbers at different times can be listed as (1) When the impragnation time is 12 hours, it is not sufficient for the contact time between the activator and the raw material (2) The 48 hour impragnation time causes the skeleton of the activated carbon to collapse. Liang et al. reported that the impragnation time should provide sufficient contact between the coal product and the activator in the synthesis of activated carbon using a KOH activator in the presence of coconut shell [21].

4. Conclusions

In this study, activated carbon was synthesized by chemical activation method using $ZnCl_2$ activator in the presence of hydrochar obtained from chickpea stalk by hydrothermal method. The characterization of synthesized activated carbon was determined by different analyzes such as SEM, FTIR and BET surface area. It was determined that the BET surface area of activated carbon was 572 m^2/g and the microporous surface area was 362 m^2/g. In the synthesis of activated carbon, the effects of important parameters such as impragnation rate, impragnation time, activation temperature and activation time were discussed. The highest iodine number of the synthesized activated carbon was determined as 734 mg / g under the conditions of impragnation time (24 hours), impragnation rate (1/2), activation temperature (400 ^oC) and activation time (45 minutes). The methylene blue number of activated carbon and hydrochar were obtained as 105 mg/g and 45 mg/g, respectively. In the present study, activated carbon, a microporous and high value-added product, was synthesized from an agricultural waste such as chickpea stalk under the light of different parameters.

References

[1] O. Baytar, Acta Chimica Slovenica **65**(2), 407 (2018).
[2] H. Sayğılı, G. A. Sayğılı, Journal of Cleaner Production **226**, 968 (2019).

[3] I. Demir, H. Li, Y. Robin, R. McClintock, S. Elagoz, M. Razeghi, Journal of Physics D: Applied Physics**51**, 085104 (2018)
[4] H. Demir, Ö. Şahin, O. Baytar, S. Horoz, Journal of Materials Science: Materials in Electronics **31**, 10347 (2020)
[5] R. T. Ayinla, J. Dennis, H. Zaid, Y. Sanusi, F. Usman, L. Adebayo, Journal of cleaner production **229**, 1427 (2019).
[6] E. Batur, O. Baytar, S. Kutluay, S. Horoz, Ö. Şahin, Environmental Technology **42**, 505 (2021).
[7] M. Erdoğan, S. Horoz, Journal of Chemical Research**45**, 207 (2021)
[8] Ş. Ö.Teğin, Ö. Şahin, O. Baytar, M. S. Izgi, International Journal of Chemistry and Technology **4**(2), 130.
[9] I. Altuntas, M. N. Kocak, G. Yolcu, H. F. Budak, A. E. Kasapoğlu, S. Horoz, E. Gür, I. Demir, Materials Science in Semiconductor Processing**127**,105733 (2021).
[10] M. Danish, T. Ahmad, Renewable and Sustainable Energy Reviews **87**, 1 (2018). [11] H. Sayğılı, G. A. Sayğılı, Journal of Cleaner Production **226**, 968 (2019).
[12] N. Zhang, Y. Shen, Bioresource technology **284**, 325 (2019).
[13] M. C. Rillig, M. Wagner, M. Salem, P. M. Antunes, C. George, H.-G. Ramke, M.-M. Titirici, M. Antonietti, Applied Soil Ecology **45**(3), 238 (2010).
[14] T. Wang, Y. Zhai, Y. Zhu, C. Li, G. Zeng, Renewable and Sustainable Energy Reviews **90**, 223 (2018).
[15] U. Karadavut, Ö. Sözen, Türk Tarım ve Doğa Bilimleri Dergisi **7**, 904 (2020).
[16] M. A. Islam, M. Ahmed, W. Khanday, M. Asif, B. Hameed, Ecotoxicology and environmental safety **138**, 279 (2017).
[17] O. Üner, Ü. Geçgel, Y. Bayrak, Arabian Journal of Chemistry **12**(8), 3621 (2019).
[18] Z. Teimouri, A. Salem, S. Salem, Environmental Science and Pollution Research **26**(8), 7718 (2019).
[19] Ö.Akçakal, M. Şahin, M. Erdem, Chemical Engineering Communications **206**(7), 888 (2019).
[20] A.El Nemr, A. G.M. Shoaib, A. El Sikaily, A. El-Deen A Mohamed, A. F. Hassan, Environmental Processes **8,** 311 (2021)
[21] Q. Liang, Y. Liu, M. Chen, L. Ma, B. Yang, L. Li, Q. Liu, Materials Chemistry and Physics **241**, 122327 (2020).