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Research Article

Preparation and characterization of activated carbon from almond shell by microwave-assisted using $ZnCl_2$ activator

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ABSTRACT

Microwave-assisted activated carbon was synthesized from almond shell by chemical activation method using $ZnCl_2$ activator. The effects of the microwave gas medium, microwave power, microwave time, activation temperature, activation time and impregnation ratio on the synthesis were investigated. Actived carbon was also synthesized in the same way without the microwave treatment. The characterization of the synthesized actived carbons was performed by SEM, FTIR and BET devices. The iodine number of the microwave assisted activated carbon (70% activator/raw material ratio, 250 W microwave power, 15 min microwave time, 500°C activation temperature and 45 min activation time) and activated carbon without microwave (70% activator/raw material ratio, 500°C activation temperature and 45 min. activation time) were determined to be 1141 mg/g and 190 mg g^{-1}, respectively. The BET surface areas of microwave assisted activated carbon and without microwave were determined as 1057 m^2 g^{-1} and 50 m^2 g^{-1}, respectively. The methylene blue numbers of the microwave assisted activated carbon and activated carbon without microwave were determined to be 201.40 mg g^{-1} and 97.14 mg g^{-1}, respectively. According these values, it can be said that the microwave process has a significant effect on activated carbon production.

Keywords: Microwave, activated carbon, chemical activation, iodine number.

$ZnCI_2$ kullanılarak badem kabuğundan mikrodalga destekli aktif karbon üretimi ve karakterizasyonu

ÖZ

$ZnCI_2$ aktifleştiricisi kullanılarak kimyasal aktivasyon yöntemiyle badem kabuğundan mikrodalga destekli aktif karbon sentezlenmiştir. Sentez üzerine mikrodalga gaz ortamı, mikrodalga gücü, mikrodalga süresi, aktivasyon sıcaklığı, aktivasyon süresi ve impragnasyon oranı etkisi incelenmiştir. Aynı yöntemle mikrodalga olmaksızın aktif karbon da sentezlenmiştir. Sentezlenen aktif karbonların karakterizasyonu SEM, FTIR ve BET cihazlarıyla gerçekleştirilmiştir. Mikrodalga destekli aktif karbon (%70 aktifleştirici/hammadde oranı, 250 W mikrodalga gücü, 15 dk. mikrodalga süresi, 500 oC aktivasyon sıcaklığı ve 45 dk. aktivasyon süresi) ve mikrodalga olmaksızın aktif karbon (%70 aktifleştirici/hammadde oranı, 500°C aktivasyon sıcaklığı ve 45 dk. aktivasyon süresi) iyot sayıları sırasıyla 1141 mg g^{-1} ve 190 mg g^{-1} olduğu belirlenmiştir. Mikrodalga destekli ve mikrodalga olmaksızın aktif karbonların BET yüzey alanları nın sırasıyla 1057 m^2 g^{-1} ve 50 m^2 g^{-1} olduğu belirlenmiştir. Mikrodalga destekli ve mikrodalga olmaksızın aktif karbonların metilen mavisi sayılarının sırasıyla 201,40 mg g^{-1} ve 97,14 mg g^{-1} olduğu belirlenmiştir. Bu değerlere göre, mikrodalga işleminin aktif karbon üretiminde ciddi bir etkiye sahip olduğu söylenebilir.

Anahtar Kelimeler: Mikrodalga, aktif karbon, kimyasal aktivasyon, iyot sayısı.

1. INTRODUCTION

Activated carbon is an excellent adsorbent used to remove various impurities. It has various advantages such as possesing high surface area, well developed internal structure and various functional groups.[1] Despite the advantages of the activated carbon adsorption process, the greatest obstacle in its wider applications is the long pyrolysis time and the provision of large devices that require high energy for biomass

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types.[2] The inclination of unsuitable heating rates impedes active carbon quality. Therefore, a fast and easy method must be developed to prepare activated carbon.[3]

Two different methods are generally used to synthesize activated carbon. These methods are known as physical activation and chemical activation. Physical activation is the activation of raw material with carbon dioxide (CO_2) or water vapor.[4] Chemical activation consists of a single step and involves the usage of activators such as zinc chloride ($ZnCl_2$), potassium hydroxide (KOH), potassium carbonate (K_2CO_3) and phosphoric acid (H_3PO_4). The carbon percentage of the chemical activation method is higher than that of the physical activation.[5] In addition, the best developed porous activated carbons are obtained via chemical activation.[6] Activated carbon can be produced from many raw materials. Examples include pistachio shell,[7] *Elaeagnus angustifolia* seeds,[8] carob bean seed husk,[9] almond shell,[10] and sunflower husk.[11]

Almond (Prunus amygdalus L.), a hard-shelled fruit that is grown in almost every region of the world, belongs to the genus Prunus of the Rosaceae family of Rosales.[12] There are approximately 40 different types of almonds. The almond fruit has an important place in human nutrition due to its high nutritional value. In addition, almond shells, which are abundant and low-cost residues, are suitable for being used as raw materials.[13] As it is consumed for its nourishing oil, rich minerals and vitamins, its production is increasing day by day. The average annual production of almonds is 80,000 tons in Turkey.[14]

Microwave technology has attracted attention because it provides homogeneous and fast thermal reactions. Microwave heating provides many advantages such as improved reaction rates and yields, performing reactions at lower temperatures, obtaining better structural properties, rapid temperature rise and uniform temperature distribution.[15] In addition, microwave technology has been used successfully to synthesize activated carbon. Impragnation process in the microwave environment in the production of activated carbon from almond shell is not available in the literature, and was first performed in this study. In the microwave-assisted activated carbon studies given in the literature, the activation process takes place in the microwave environment. In this study, the impragnation process was carried out in the microwave environment.

In our study, activated carbon synthesized by the microwave assisted chemical activation method was obtained from almond shells. The BET surface areas of microwave assisted activated carbon and without microwave were determined respectively. When the iodine number, methylene blue number and BET surface area numbers were taken into consideration, it was observed that microwave treatment had a significant effect on the production of activated carbon.

2. MATERIALS AND METHODS

2.1. Materials

All chemical materials used in the experimental studies were obtained from Merck and were of analytical purity. Deionized pure water was used in the experimental studies. Almond shells were obtained from the province of Siirt, Turkey. The system used to synthesize the activated carbon is given in Figure 1. The system consists of a microwave and horizontal ash oven.

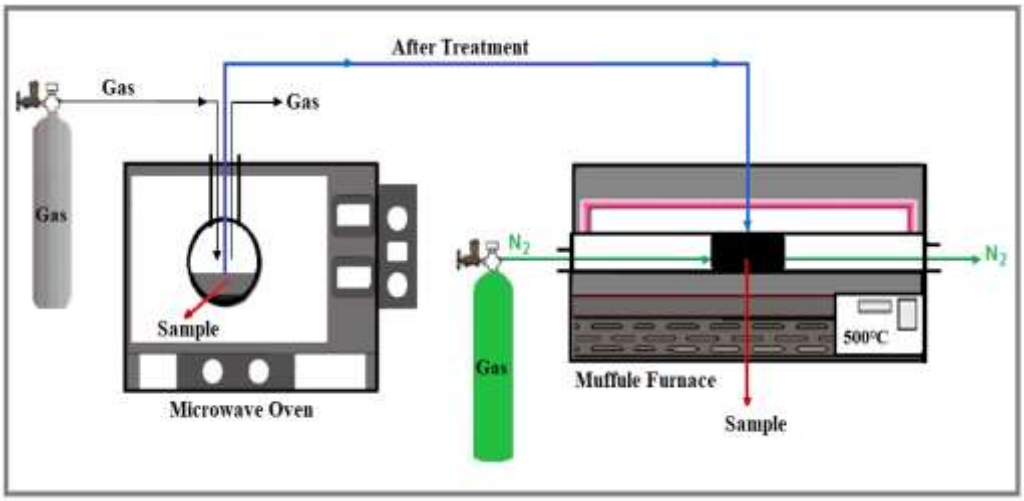

Figure 1. System used for the production of activated carbon.

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2.2. Synthesis of activated carbon

The almond shells were milled and sieved, then washed with distilled water and dried at 80°C. Activated carbon was synthesized by the microwave assisted chemical activation method. For the synthesis of the activated carbon, 3 g of ground almond shells were mixed with 3 g of $ZnCl_2$ activator dissolved in 2 ml of distilled water and the impregnation of the activator into the almond shells was carried out in a microwave. In the microwave environment, the activated carbon was synthesized by subjecting the activation time to 45 min at 500°C in the presence of nitrogen (N_2). The activated carbon washed with 0.5 M hydrogen chloride (HCl) and then hot distilled water until the pH value was 6-7.

2.3. Characterization of activated carbon

The iodine number of the active carbons obtained was determined. Iodine adsorption is performed to learn more about the porous structure of activated carbon. Iodine adsorption in the liquid phase is considered as a simple and rapid test. The iodine number is determined by the surface area of the pores with a radius greater than 1 nm. The iodine number is accepted as a basic parameter used to characterize the performance of activated carbon.[7] The method used by the International American Society of Testing and Materials was used to determine the iodine number (ASTM, 2006). The iodine number was calculated using Eq. (1).

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

Where, A is the amount of $Na_2S_2O_3.5H_2O$ spent in titration after activated carbon iodine adsorption (ml). B is amount of $Na_2S_2O_3.5H_2O$ spent in titration for 0.1 N iodine solution (ml). N is iodine solution concentration. m is the amount of activated carbon (g).

In the synthesis of activated carbon, iodine number is used as an alternative to the BET surface area in the laboratory environment. For this reason, the iodine number of all activated carbons obtained was determined and plotted. The activated carbon with the highest iodine number was sent to BET analysis

The BET surface area of the activated carbons with high iodine number was determined by the Quantachrome Nova 1200 series device. The characterization of the activated carbon with the highest surface area, pure almond shell and non-microwave activated activated carbon, scanning electron microscopy (SEM), and fourier-transform infrared spectroscopy (FTIR) devices were performed and methylene blue number were determined. The methylene blue number was used to estimate mesoporosity of activated carbons. A good quality activated carbon should have high iodine number and methylene blue number.[7]

The number of methylene blue was calculated from Eq. (2).

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

Where, q_e is the amount of methylene blue adsorbed per unit adsorbent (mg g^{-1}). C_o is solution initial concentration (mg l^{-1}). C_e is the concentration of solution in equilibrium state (mg l^{-1}). V is solution volume (ml). w is the amount of adsorbent (g).

3. RESULTS AND DISCUSSIONS

The SEM images of the almond shell, microwave assisted activated carbon and without the microwave treatment are given in Figure 2 (a-c), respectively.

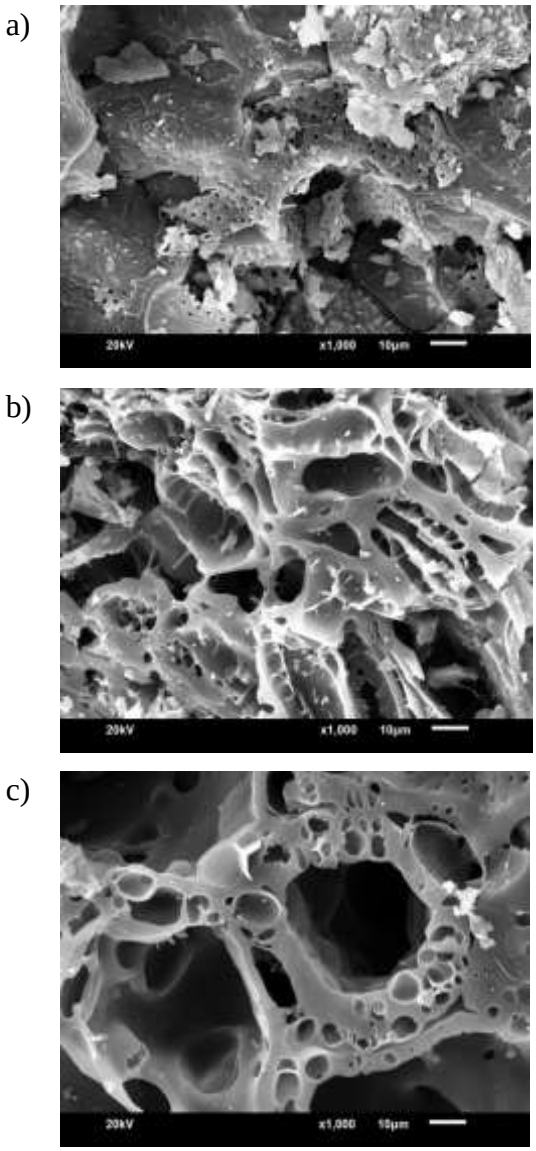

Figure 2. SEM image of: a) Pure almond shell, b) Microwave assisted activated carbon, c) Activated carbon without the microwave treatment.

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As can be seen from Figure 2a, the surface of the pure almond shell was rough, although not very porous. The surface of the microwave assisted activated carbon appears to be porous and flat (Figure 2b). It is seen from Figure 2b that the microwave-assisted activated carbon surface was more porous and smooth compared to the almond shell. As can be seen from Figure 2, the microwave causes the activated carbon to form a micropore structure. In addition, it was observed that the micropores of the microwave-assisted activated carbon were greater than those of the activated carbon without the microwave treatment.

The BET surface area analysis of the synthesized actived carbon with high iodine numbers was performed and the results obtained are given in Figure 3.

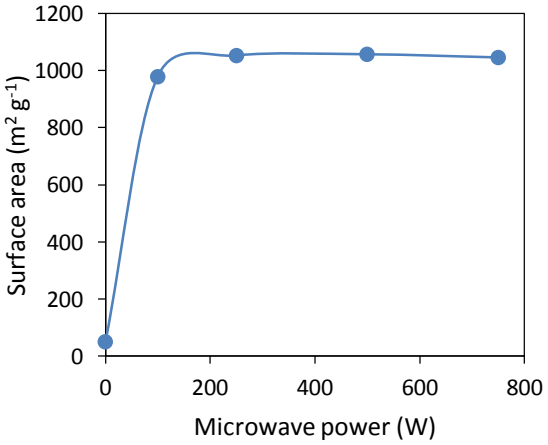

Figure 3. Variation of microwave power with surface area.

Figure 3 shows that the surface area of the activated carbon impregnated in the microwave was 1057 m^2 g^{-1}, while the surface area of the activated carbon not impregnated in the microwave was 50 m^2 g^{-1}. The effect of the microwave power on the impragnation of activated carbon is clearly seen from the BET surface area data.

The FTIR spectra of almond shell, microwave assisted and without microwave activated carbon are given in Figures 4a-c, respectively.

It is seen that there are more than one functional group in the structure of the almond shell. Figure 4 shows the presence of the OH-functional group connected to the peak hydrogen bonds at 3700 cm^{-1} wavenumber. It shows the presence of C-H functional group due to peak methyl groups at 3000 cm^{-1}.[2, 16] The peak at 2300 cm^{-1} indicates the presence of the -C00H functional group. It shows the presence of C-C bonds due to peak olefenic groups at 2000-1800 cm^{-1}. It shows the presence of the peak CH_2 functional group at 1500 cm^{-1}.

The peak at 1266 cm^{-1} shows the presence of C-C and C-O functional groups. The peaks smaller than 1000 cm^{-1} indicate the presence of functional groups resulting from the aromatic ring.

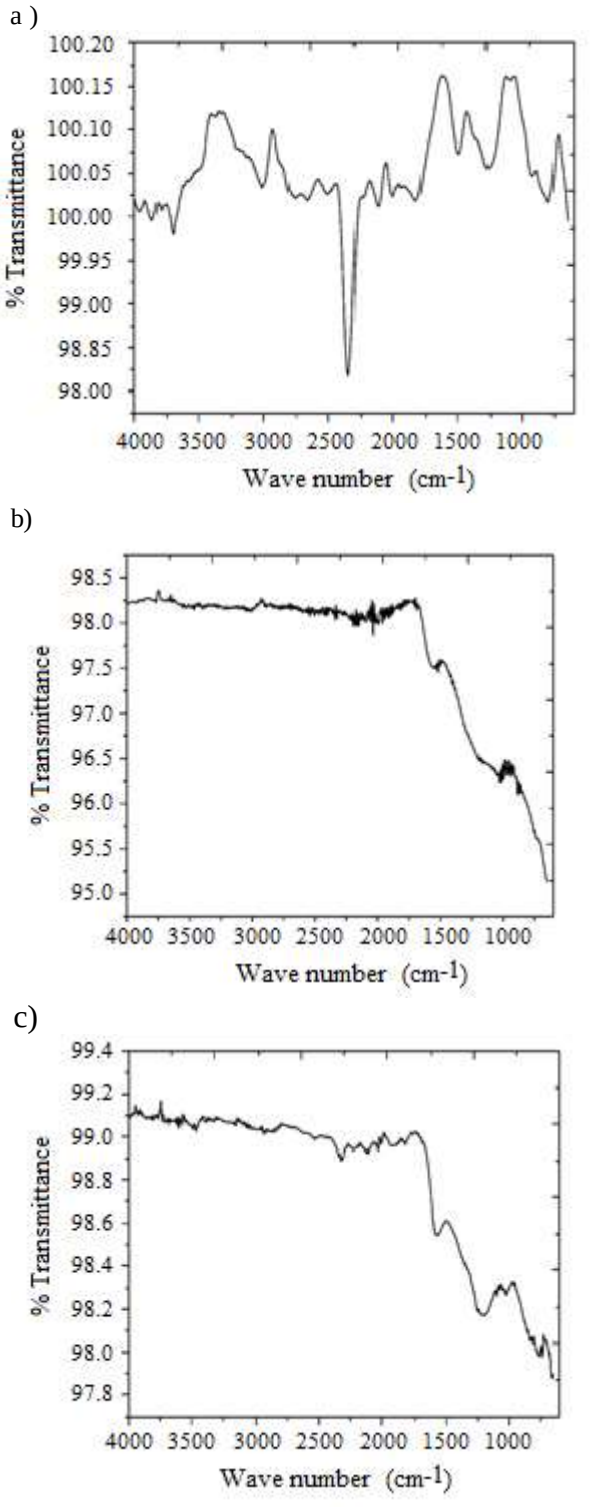

Figure 4. FTIR graphs: a) Raw material, b) Microwave assisted activated carbon; c) Activated carbon without microwave.

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It can be seen from Figure 4 that although there are many functional groups in the structure of the pure almond shell, there are not many functional groups in the structure of the activated carbon synthesized with microwave treatment. The probable reason for this is that the microwave power weakens the bonds formed between the activator and the raw material. The functional groups in the actived carbon structure, which were synthesized without microwave treatment, are more than the functional groups in the microwave-assisted activated carbon structure. These results support the idea that microwave power weakens the bonds between the raw material and the activator.

Methylene blue number of microwave assisted activated carbon and without microwave was determined as 201.40 mg/g and 97.14 mg g^{-1}, respectively. The high methylene blue number indicates that activated carbon is mesoporous.[17] Microwave-assisted activated carbon seems mesoporous in the SEM images also.

Impregnation ratio is one of the most important parameters in the preparation of activated carbon. The effect of impregnation ratio was investigated under the conditions of 750 W microwave power, 15 min microwave time, 500°C activation temperature and 45 min activation time. The experiments were performed at impregnation ratios of 20%, 50%, 70%, 100% and 150% . The variation of iodine numbers with the ratio of impregnation is given in Figure 5.

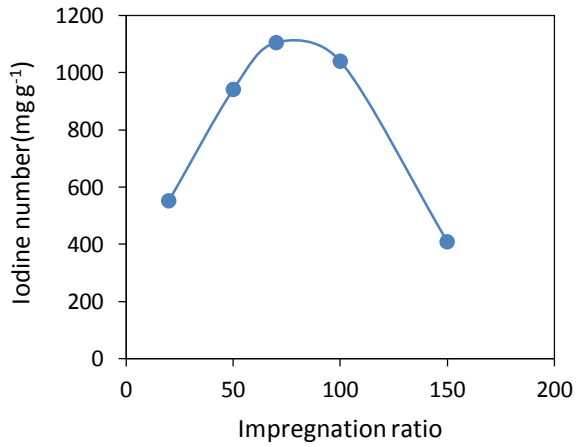

Figure 5. Variation of iodine number according to impragnation ratio(microwave power 750 W; microwave time 15 min.; activation temperature 500°C; activation time 45 min. and CO_2).

It is seen that iodine number increases with the increase of the impregnation ratio from 20% to 70%, while the iodine number decreases when the impragnation ratio become greater than 70%. There are two possible reasons for this. First, when the amount of activator is low, it does not fully activate with raw material. Secondly, when the amount of activator is high, the activated carbon causes the pores to have a macro structure. Şahin and co-workers[8] have found the same result on the activated carbon obtained by the chemical activation method using the $ZnCl_2$ activator from the spindle nucleus. In their studies, the best impregnation ratio has been determined to be 70% and used in subsequent experiments. Liu and co-workers have found that the impragnation rate of activated carbon which they have obtained from bamboo using phosphoric acid, was 100%.[18]

After determining the best impragmentation ratio, the effect of different gases on the microwave environment was investigated under 70% impregnation ratio, 750 W microwave power, 15 min microwave time, 500°C activation time and 45 min activation time. The iodine numbers of activated carbons obtained are given in Table 1.

Table 1. The effect of different gases on iodine number

Gas	Iodine number
CO_2	1105
N_2	1011
Ar	1024

The iodine number of the activated carbon obtained in the presence of CO_2 was higher. The possible reason for this is thought to be the weakening of the bonds between the activator and the raw material in the presence of CO_2 by the microwave. The CO_2 gas was used to examine the effect of other parameters. Sharif and co-workers have found that CO_2 gas in microwave environment is effective in the activated carbon they have obtained from sesame stem with microwave support. The probable cause of this situation is that they have stated that carbon dioxide has reacted with more pores formed during the pyrolysis process.[19]

The effect of microwave power was investigated under 15 min microwave time, CO_2 gas environment, 500°C activation temperature and 45 min activation time. The variation of iodine number of activated carbons by microwave power is given in Figure 6.

It is observed that the iodine number increases when the microwave power increases from 100 W to 250 W. However, when the microwave power became greater than 250 W, the iodine number decreased. This may be due to the fact that the bond between the activator and the raw material is completely weakened when the microwave power is 250 W.

It is also thought that the viscosity of the activator was reduced with microwave heat and therefore, better penetration into the interior of the activating raw

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material occurred. When the microwave power was below 250 W, the activator did not penetrate well into the inner side of the raw material as it did not reduce the viscosity of the activator. When the microwave power is low, it is thought that it does not weaken the bonds between the activator and the raw material. For these reasons, the iodine number was chosen to be low. When the microwave power was above 250 W, the viscosity of the activator greatly increased and, as a result, the pore structure of the raw material caused macro formation.

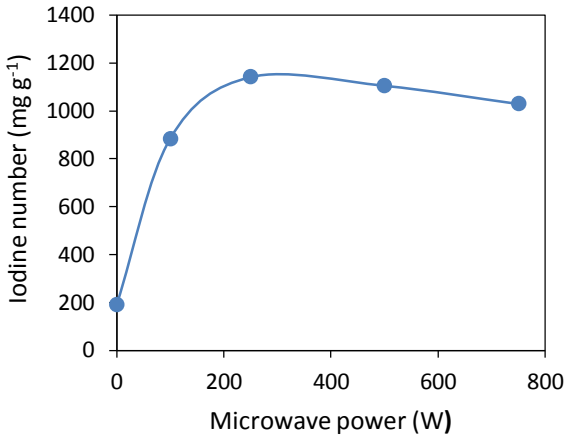

Figure 6. Variation of iodine number according to microwave power (impregnation ratio 1:1; microwave time 15 min; activation temperature 500°C; activation time 45 min and CO_2).

The effect of the microwave time was investigated under the 250 W microwave power, CO_2 gas environment, 500 °C activation temperature and 45 min activation time. The change in the iodine numbers of activated carbons with microwave power is graphed in Figure 7.

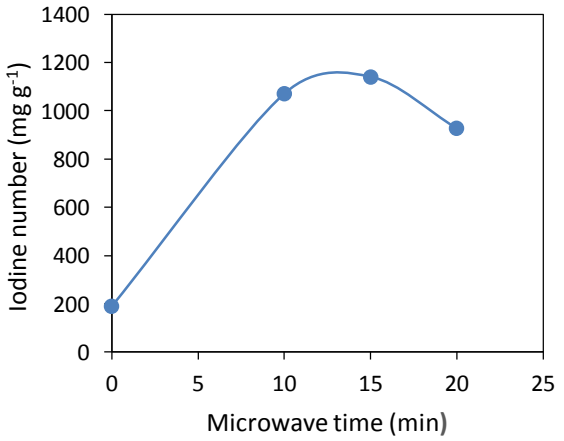

Figure 7. The change in the iodine numbers of activated carbons with microwave time (impregnation ratio 1:1; microwave power 250 W; activation temperature 500°C; activation time 45 min and CO_2).

When the microwave time was 10 and 15 min, the iodine number was observed as 1071 mg g^{-1} and 1141 mg g^{-1}, respectively. However, when the microwave time was 20 min, the iodine number was 927 mg g^{-1}. The reason for this is thought to be that the microwave time of 10 min did not weaken the bonds between the activator and the raw material and did not diminish the viscosity of the activator sufficiently. When the microwave time is 20 min, it is thought that the activator disrupted the structure of the raw material. In other words, the viscosity of the activator was extremely reduced and consequently the pore structure of the raw material deteriorated. The best microwave duration was determined as 15 min.

After determining the best microwave parameters, the activation parameters were determined. The effect of the activation temperature was investigated under the conditions of 250 W microwave power, CO_2 gas medium in the microwave and 45 min activation time. The variation of the iodine numbers of activated carbons with the activation temperature is graphed in Figure 8.

When the activation temperature increased from 400°C to 500°C, it can be seen that the iodine number increases and then decreases. The possible cause of this is thought to be that the activation temperature of 400°C is not sufficient to open the pores in the activated carbon structure and 500°C is suitable to open the pores. It is thought that the activation temperature of 600°C causes to transform into the micropores of the macropores of the activated carbon. The best activation temperature was determined to be 500°C. Li and co-workers had found that the activation temperature was 500°C better in the synthesis of the active they obtained from rice husk. They stated that the pore structures collapsed at 600°C.[17]

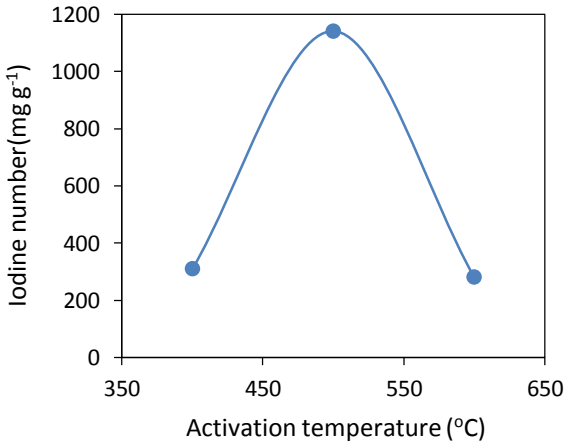

Figure 8. The variation of the iodine numbers of activated carbons with the activation temperature (impregnation ratio 1:1; microwave power 250 W; microwave time 15 min; activation time 45 min and CO_2).

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The effect of activation time was investigated under 250 W microwave power, CO_2 gas environment and 500°C activation temperature. The change in the iodine number of the activated carbons with the activation time is graphed in Figure 9.

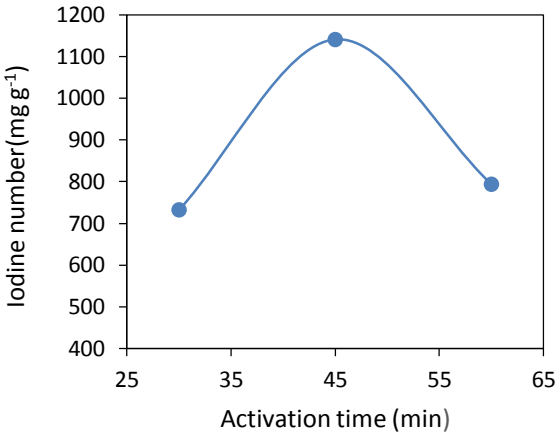

Figure 9. The change in the iodine number of the activated carbon with the activation time (impregnation ratio 1:1; microwave power 250 W; microwave time 15 min; activation temperature 500°C and CO_2).

When the activation time was 30, 45 and 60 min, the iodine number was determined to be 732 mg g^{-1}, 1141 mg g^{-1} and 794 mg g^{-1}, respectively. This may be due to the fact that the activation time of 30 min is not sufficient to fully open the pores of activated carbon. When the activation time is 60 min, it is thought that the activated carbon pores turns into mesopores and the pore structure of activated carbon collapse. Özdemir and co-workers have found that the activation time in the activated carbon they obtained from grape stem using $ZnCI_2$ activator was 120 minutes at best.[20]

4. CONCLUSIONS

In this study, microwave assisted activated carbon was synthesized from almond shell. In the synthesis of the activated carbon, the effects of different parameters such as gas medium, microwave power, microwave time, activation temperature, activation time and impregnation ratio in the microwave were investigated. The characterization of the synthesized activated carbons was carried out by SEM, BET and FTIR. The iodine numbers and methylene blue numbers of the synthesized activated carbons were determined. The iodine number of the microwave assisted activated carbon (70% activator/raw material ratio, 250 W microwave power, 15 min. microwave time, 500°C activation temperature and 45 min activation time) and activated carbon without microwave (70% activator/raw material ratio, 500°C activation temperature and 45 min activation time) were determined to be 1141 mg/g and 190 mg/g, respectively. The BET surface area values of microwave assisted (70% activator/raw material ratio, 250 W microwave power, 15 min. microwave time, 500°C activation temperature and 45 min activation time) and without microwave activated carbon (70% activator/raw material ratio, 500°C activation temperature and 45 min. activation time) were determined to be 1105 m^2 g^{-1} and 190 m^2 g^{-1}, respectively. The optimum conditions required to obtain activated carbon with the highest surface area can be listed as follows: CO_2 gas medium, 250 W microwave power, 15 min microwave time, 500°C activation temperature, 45 min activation time and 70% impregnation ratio. In previous studies in the literature, the microwave activation process was used in the synthesis of activated carbon with and without microwave treatment. Unlike these studies, microwave impragnation was applied in the present study. The BET surface area and iodine numbers show that microwave had a significant effect on the impregnation process.

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Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

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