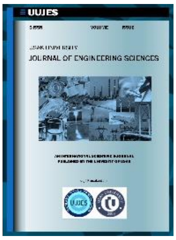

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Research article

THE EFFECT OF PRE-WASHING PROCESS WITH NaOH SOLUTION ON THE SURFACE AREA IN ACTIVATED CARBON PRODUCTION

Gülser KARAKOÇ[1], Feyyaz KESKİN[2], Çiğdem Elif DEMİRCİ[3], Selçuk AKTÜRK[4]*

[1] *Muğla Sıtkı Koçman University, Graduate School of Natural and Applied Sciences, Department of Physics, Muğla, Türkiye*

[2] *Muğla Sıtkı Koçman University, Environmental Problems Research and Application Center, Muğla, Türkiye*

[3] *Muğla Sıtkı Koçman University, Research Laboratories Application and Research Center, Muğla, Türkiye*

4 Muğla Sıtkı Koçman University, Faculty of Science, Department of Physics, Muğla, Türkiye

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Abstract

The alkaline pre-washing process in the production of activated carbon is an important step and a factor that affects the characteristics of activated carbon. Alkaline pre-washing is used to optimize the surface properties of activated carbon, increase its adsorption capacity, and remove unwanted substances.

In this study, hazelnut shells were selected as the raw material for producing activated carbon. ZnCl2 was used for chemical activation, and physical activation was carried out at 650 °C. However, prior to the chemical activation process, a pre-washing process with NaOH solution was applied to remove acidic groups present in the raw material. The structural properties of the activated carbon obtained from samples subjected to the pre-washing process and those without the pre-washing process were determined using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) for surface morphology, Brunauer-Emmet-Teller (BET) for pore size analysis, and Thermogravimetric Analysis (TGA) for temperature-dependent mass loss.

The surface area of the activated carbon produced without pre-washing with NaOH solution was found to be 770 m^2/g, with a carbon content of 87.10% by weight. After the pre-washing process with NaOH solution and subsequent chemical and physical activation, the surface area of the activated carbon increased to 1935 m^2/g, with a carbon content of 95.51% by weight. Therefore, subjecting the raw material to the pre-washing process with NaOH solution not only increased the carbon content but also increased the surface area value by approximately 2.5 times.

Keywords:. *Activated Carbon; Alkaline Pre-washing; Surface Area; Carbon Content*

*Corresponding author: Selçuk AKTÜRK
E-mail: selcukakturk@mu.edu.tr (ORCID: 0000-0001-9146-5142)

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1. Introduction

Activated carbon is a highly porous form of carbon that is known for its ability to adsorb organic substances, gases, and pollutants [1]. Due to its high adsorption capacity and surface area, activated carbon is widely used in various industrial applications [2]. It is a versatile material that can find applications in many fields such as energy, mining, environment, agriculture, health, cosmetics, and defense industry [3]. It is used to remove organic pollutants, compounds that cause odor and taste, chlorine, and other harmful substances in water treatment systems [4,5]. Activated carbon filters are used in various applications ranging from residential water treatment systems to industrial water treatment plants. It is also effective in removing gases and volatile organic compounds in air purification systems [6]. These systems adsorb harmful gases originating from various sources such as chemical processes, industrial waste gases, and air pollution [7]. Additionally, it is used in various applications in the chemical industry [8]. It can be used as catalyst carriers, purification of solvents, gas storage and separation processes, pharmaceutical production, and other chemical processes [3,9]. Activated carbon is typically produced using raw materials such as plant-derived materials, wood, coconut shell, and coal [10,11]. These materials are prepared in a suitable form by grinding and drying [12]. The prepared raw material is heated in a carbonization furnace at high temperatures (usually between 600-900 °C) [13,14]. In this process, water, volatile organic compounds, and combustible gases are removed from the material, and it is converted into carbon [15]. After carbonization, the carbon is brought into contact with a predetermined activating agent. These agents can include substances such as water vapor, carbon dioxide, potassium hydroxide, or phosphoric acid [16]. Subsequently, the applied activation process improves the pore structure and increases the surface area of the material [17]. After the activation process, activated carbon is washed and cleaned [18]. This step is performed to remove residues, by-products, and activation agents [18,19]. Then, the activated carbon is dried. The combination of these steps constitutes the production process of activated carbon. The parameters used in the production process can vary depending on the raw material, activating agent, and application requirements [20]. Environmental, economic, and functional parameters are important considerations in the preparation of activated carbon [16,21,22]. In a literature review, Lillo-Rodenas et al. achieved highly porous activated carbon with a BET specific surface area of 2746 m^2/g [23]. Subsequently, from 2003 to 2005, some researchers reported that the reaction mechanism of NaOH is similar to that of KOH, and the same highly porous activated carbon can be obtained using NaOH activation [24-30]. The above-mentioned studies have revealed the beneficial use of NaOH activation in the preparation of activated carbon. NaOH activation in the production of activated carbon is generally performed after the carbonization step [31]. There is not enough information in the literature about applying activation with NaOH to the starting raw material before carbonization to obtain activated carbon. In this study, hazelnut shell was used as the raw material to obtain activated carbon. The changes in the surface area and carbon content of the activated carbon were investigated by washing with NaOH alkaline solution before the chemical activation step using $ZnCl_2$.

2. Materials and Method

In this study, activated carbon production was carried out using hazelnut shell as the raw material through two different production processes. The produced activated carbon was subjected to Thermogravimetric Analysis using a PERKIN ELMER TGA 4000 model device. X-ray diffraction patterns were determined using the RIGAKU SMARTLAB X-RAY

(XRD) system, surface images were obtained using the JEOL JSM-7600F (FE) Scanning Electron Microscope (SEM), and element analysis was performed using the Oxford Ins. EDS attached to the SEM system. BET surface area determination was carried out using the MICROMERITICS GEMINI VII 2390t device.

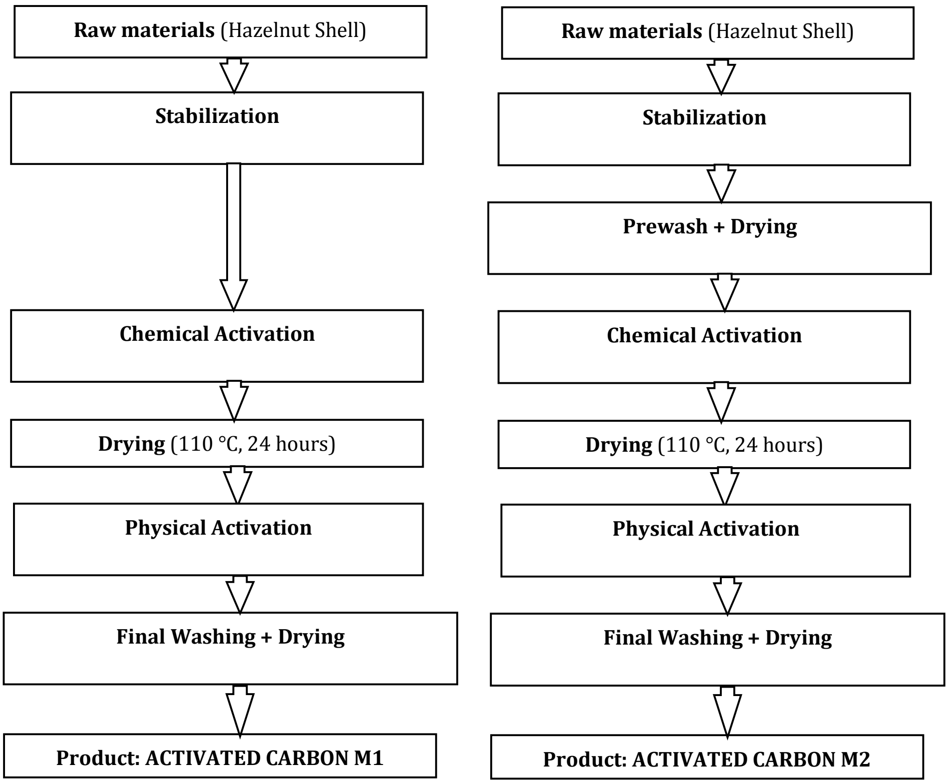
Firstly, 10g of raw hazelnut shell was mixed with 30ml of pure water at room temperature for 24 hours, and the pH value of the solution was determined to be 4.1. Then, the following methods were applied. Method 1 used in activated carbon production: The hazelnut shell raw material was first ground and kept in an oven at 60°C for 1 hour. Then, it was treated with $ZnCl_2$ in a magnetic stirrer at 80°C for 3 hours and left to dry for 24 hours at 110°C. Subsequently, a physical activation process was applied at 650°C for 1 hour under N_2 atmosphere. After physical activation, the samples were soaked in a 0.5M HCl solution. In the final step, they were washed with pure water at 70°C until the pH value reached 7. Method 2 used in activated carbon production: The hazelnut shell raw material was first ground, kept in an oven at 60°C for 1 hour, and mixed with a 0.5M NaOH solution for 24 hours at room temperature. Then, it was washed with pure water at 70°C until the pH value reached 7. It was treated with $ZnCl_2$ in a magnetic stirrer at 80°C for 1 hour and left to dry for 24 hours at 110°C. Subsequently, a physical activation process was applied at 650°C for 1 hour under N_2 atmosphere. After physical activation, the samples were soaked in a 0.5M HCl solution. In the final step, they were washed with pure water at 70°C until the pH value reached 7. The two production methods used in activated carbon production (Method 1 and Method 2) are shown in Table 1. The sample obtained using Method 1 was labeled as M1, and the sample obtained using Method 2 was labeled as M2.

3. Results and discussion

The XRD patterns of sample M1 obtained from Method 1 and sample M2 obtained from Method 2 in the production of activated carbon are shown in Figure 1a and Figure 1b, respectively. Upon examination of the XRD results, it was determined that both samples exhibited an amorphous structure. The presence of an amorphous structure indicates that they do not possess a crystalline structure. Activated carbon is typically amorphous because the activation process disrupts the carbon's crystalline structures and creates a large surface area and pore structure. Therefore, the amorphous structure is an expected characteristic in the XRD results.

The surface characteristics of the samples M1 and M2, which were determined to have an amorphous structure, were investigated using SEM, and the results are presented in Figure 2. Figure 2a shows the SEM images and EDS spectra of the M1 sample, while Figure 2b shows those of the M2 sample. Based on the SEM analysis, it is evident that the pore morphologies are similar to each other. The overall EDS analysis results obtained from the region where SEM images were taken for samples M1 and M2 are presented in Table 2. According to Table 2, it can be observed that the carbon (C) content in the M2 sample is higher compared to the M1 sample. The EDS analysis also indicates that there are no significant impurities present in the structure. This result supports the findings of the XRD analysis.

Table 1. Activated Carbon Production Methods



a) **b)**

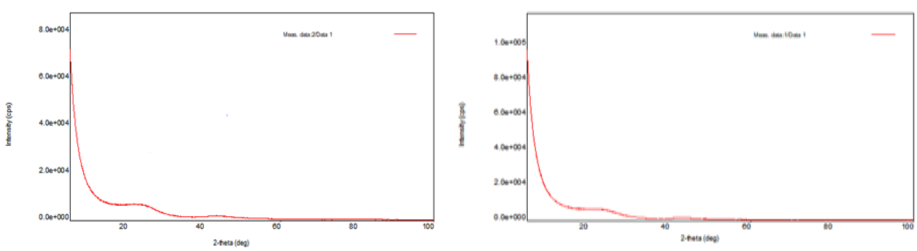


Fig. 1a **Fig. 1b**

Fig1. (a) XRD patterns of M1 and **(b)** XRD patterns of M2

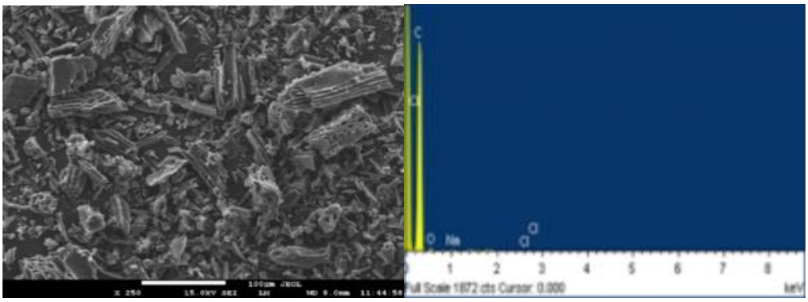


Fig. 2(a)

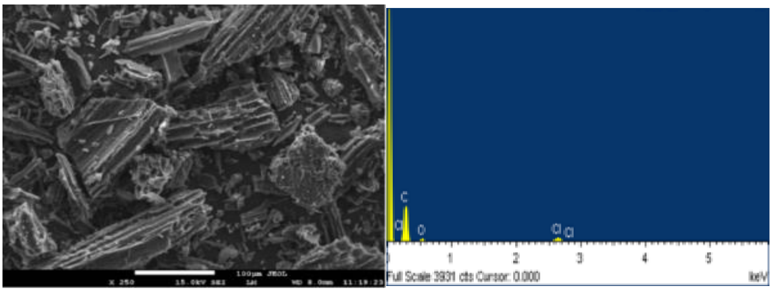


Fig.2(b)

Fig. 2 SEM images and EDS spectra of samples **(a)** M1 and **(b)** M2.

Table 2 EDS elemental analysis results for samples M1 and M2.

	M1	M1	M2	M2
Element	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	81,45	87,1	94,06	95,51
O	14,26	11,44	5,81	4,43
Na	0	0	0,05	0.02
Cl	4,29	1.55	0.08	0.03

The effect of pre-washing with NaOH on the temperature-dependent mass loss of the resulting product in the production of activated carbon has also been investigated. TGA curves of the untreated raw hazelnut shell, M1 sample, and M2 sample are shown in Figure 3. It has been determined that the highest mass loss occurs in the raw sample, while the lowest mass loss is observed in the M2 sample subjected to pre-treatment with NaOH.

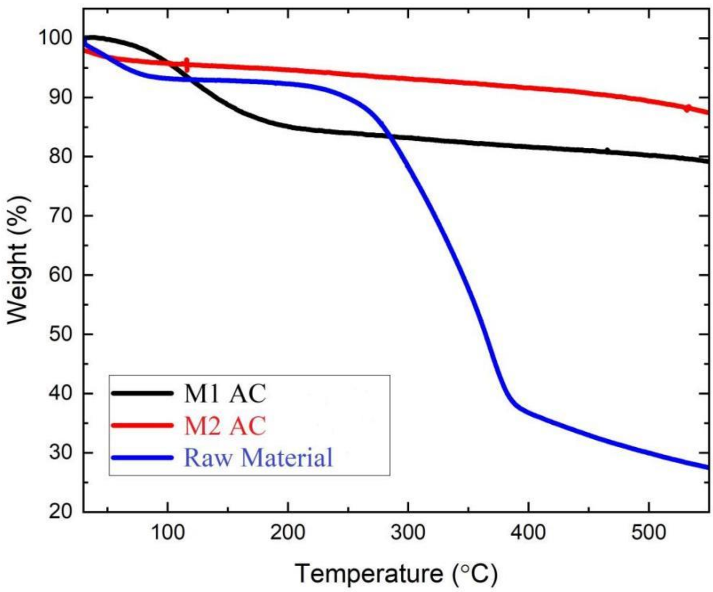


Fig. 3 TGA data of the raw sample, M1, and M2 samples.

The BET surface areas of M1 and M2 samples were investigated, and it was determined that the surface areas of M1 and M2 samples were 770 m^2/g and 1935 m^2/g, respectively. The obtained BET surface area data indicates that the surface area of activated carbon produced by applying the NaOH pre-washing process is significantly higher than that of activated carbon produced without any pre-treatment. When all the results are evaluated, it is revealed that the addition of the NaOH pre-washing process to the activated carbon production process can increase the surface area of the produced activated carbon.

This value is considered high compared to many studies in the literature, suggesting a high potential for the removal of pollutants from aqueous solutions. Recent studies on activated carbon production for the removal of various chemicals or pollutants have included the use of new raw materials and activation chemicals that have not been tried before, and it has been observed that the use of hazelnut shells as a raw material was more common before 2010 but decreased afterwards. Furthermore, an increase in surface area values has been observed in the obtained results [31-35].

When examining the studies conducted using hazelnut shells as a raw material in recent years, it is understood that the surface area values of activated carbons vary significantly with different activation methods and chemicals, while they show closer values with similar methods and chemicals. Some studies conducted using this raw material have shown that the surface areas of activated carbons produced using hazelnut shells range from 314 to 1363 m^2/g [32-34]. Şencan et al. (2015) achieved an activated carbon with a BET surface area value of 736.49 m^2/g by using $ZnCl_2$ as an activator in a chemical activation method following thermal activation [32]. Zhu et al. (2016) reached a BET surface area value of 1125 m^2/g using nitrogen atmosphere in the physical activation method [33]. Livani, Ghorbani, and Mehdipour (2018) obtained activated carbon with a BET surface area of 314 m^2/g by using NaOH as an activation chemical in a chemical activation method [31]. Ozpinar et al. (2022) successfully produced activated carbons with a BET surface area value of 1363 m^2/g by using H_3PO_4 in the chemical activation process [34]. Altintig, Sarıcı, and Karataş (2023) also achieved activated carbon with a BET surface area value of 1208 m^2/g using the same activation method and activation chemical [35].

4. Conclusion

In this study, although the same chemical was used in the activation stage and the activation time in Method 1 (M1) was three times longer than in Method 2 (M2), the surface area value obtained with Method 2 is approximately 2.5 times higher than the surface area value obtained with Method 1. The alkaline pre-washing process is typically carried out using alkaline solutions such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). These solutions alter the acidic and basic groups on the surface of activated carbon, increase microporosity, and improve the adsorption properties of activated carbon [36, 37]. In this study, it was observed that the applied alkaline pre-washing process had an effect such as removing unwanted substances and improving the surface properties of activated carbon. Considering that the pH value of the starting material is acidic, pre-washing the raw material with NaOH solution ensures the removal of unwanted substances from the environment. Additionally, it was revealed that various pollutants and by-products resulting from the production process, which could negatively affect the performance of carbon, were removed, thereby enhancing the purity of activated carbon.

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