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# Removal of color material by activated carbon of some agricultural waste

Bahar Ikizoglu[a], Nazire Mazlum[b], Gurdal Kanat[c,*]

[a]*Department of Environmental Engineering, Suleyman Demirel University, 32260 Cunur, Isparta, Turkey, email: baharikizoglu@sdu.edu.tr*
[b]*Department of Environmental Engineering, Pamukkale University, 20070 Kınıklı, Denizli, Turkey, email: nmazlum@pau.edu.tr*
*cDepartment of Environmental Engineering, Yildiz Technical University, 34220 Esenler, Istanbul, Turkey, Tel.: +90 (212) 383 5393; email: kanat@yildiz.edu.tr/gkanat@gmail.com*

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**ABSTRACT**

Activated carbon is well known as a porous material and has a large specific surface area. Therefore, such a material has desirable adsorption properties and has been used for purification and elimination of hazardous components. Due to the current increased problems of environmental pollution, activated carbon is expected to play an important role in pollution abatement. This study aimed to investigate the removal of methylene blue with activated carbon produced from olive seeds, olive pomace and walnut shells. In the study, the impact of the adsorbents employed for dye adsorption was analyzed based on the initial dye concentration, contact duration and, kinetic and isotherm properties were determined based on the study findings. Analysis showed that the best pore structure was in the olive seed activated carbon and alcohols, ketones and carboxyl groups formed in activated carbon samples. The X-ray photoelectron spectroscopy findings demonstrated the highest C content was in the olive seed activated carbon sample after the commercial activated carbon. The activated carbon samples were employed to adsorb 10 mg/L methylene blue solution.

*Keywords:* Methylene blue; Adsorption; Olive seeds; Olive pomace; Walnut shells

## 1. Introduction

Recently, the employment of dyes in several industrial processes such as paper and pulp manufacturing, plastics, cloth dyeing, leather treatment and printing has increased significantly. The textile industry, which is the highest source of dyes, is among the locomotive industries especially in developing countries. The share of the Turkish textile industry in global textile production is about 4%, and the country ranks 8th. The Turkish textile industry is the second largest supplier in Europe [1,2]. According to Turkish Statistical Institute, textile industry is responsible for 15% of the overall industrial water consumption (around 200 million $m^3$/y) and it is the second largest industrial water consumer in the manufacturing industry [2,3]. Thus, contamination of water resources by the Turkish textile industry is a significant concern. Wet manufacturing processes employed in the textile industry lead to various types of waste including wastewater, chemicals/dyestuff and solid waste.

Synthetic dyes are significant organic pollutants. Approximately 10%–15% of the dyes employed in several industries are directly discharged to the nature. Thus, the discharge of toxic textile dyes to the environment affects the survival of certain organisms and aquatic life systems. Furthermore, as suggested by Malik [4], Namasivayam and Kayitha [5] the by-products of dye reactions are highly carcinogenic and mutagenic. In fact, the problem is more significant when it is considered that more than 10,000 types of dyes are employed in the world with a mean annual production of over 700,000 tons based on the Color Index [6].

* Corresponding author.

Methylene blue (MB), a cationic dyestuff, is a heterocyclic aromatic compound with significant adverse effects on plants, animals and aquatic ecosystems. Methylene blue (MB) is commonly discharged by several manufacturing and textile industries over the recommended limit, leading to water pollution and other hazards. MB ($C_{16}H_{18}C_lN_3S$) produces a deep blue color in water or alcohol. It is a greenish blue organic dye commonly employed as an indicator or a dye. It has noxious effects on human beings and may be carcinogenic due to non-biodegradable properties [7,8].

Activated carbon is among the most preferred adsorbents for the removal of dyestuff from wastewater through adsorption. However, the high cost of activated carbon accelerated the studies on the production and development of adsorbents based on different materials [9,10].

The present study aimed to investigate the removal of methylene blue, which is commonly employed in textile, leather and paper industries, has toxic effects even in very low concentrations in water. In the study, the impact of the adsorbents produced from olive seeds, olive pomace and walnut shells was analyzed based on the initial dye concentration, contact duration and, kinetic and isotherm properties were determined based on the study findings.

## 2. Material and methods

### 2.1. Preparation of walnut shells, olive seeds and pomace

The walnut shell utilized in the experiments was procured in Kirsehir Province, olive pomace and olive seeds were procured in Yatagan District, Mugla Province. The walnut shells and olive seeds that were between 1 and 4 mm were selected. The shells and seeds were crushed, washed to clean the dust. The pomace was procured in dry form. 25 g samples were weighed on a RADWAG Wagi Elektronikzne brand analytical balance.

### 2.2. Production of activated carbon

First, all walnut shells were washed with tap water to remove surface impurities. Then, they were washed with deionized water. The samples were then placed in a drying oven for 12 h, at 105°C. After the shells were dried, they were crushed into 1–2 mm with 100 mm × 100 mm particles with a jaw crusher.

#### 2.2.1. Chemical activation of food waste

Aqueous 30% $K_2CO_3$ solutions were prepared for chemical activation. Activated agent solutions were added on 25 g samples and mixed for 4 h. Then they were dried in an oven at 105°C. Later, they were mixed with 5% $H_3BO_3$ in shaking water bath for 2 h, at 80°C and 125 rpm. Then, the samples were filtered through rough filter paper, and dried in oven for 12 h, at 105°C.

In the carbonization process, activated food waste (pomace, olive seeds, walnut shell) that were placed in porcelain capsules were placed in a furnace where 15 min nitrogen gas flow was maintained before the procedure. The shells were carbonized for 60 min, at 750°C with a heating rate of 10°C/min and under a nitrogen gas flow of 1,000 mL/min. The activated carbon samples were washed until the pH value was 6–6.5. After the pH was adjusted, the samples were dried in an oven for 12 h at 105°C. The dried granulated active carbon samples were grinded and preserved to prevent humidity.

### 2.3. Methylene blue experiment

Three methylene blue solution concentrations, namely 0.5, 5 and 10 mg/L, were prepared and their absorbances were measured individually with a spectrophotometer. To determine the activated carbon performance, 0.1, 0.3 and 0.5 g activated carbon samples were weighed on an analytical balance. For the performance test, 50 mL 10 mg/L methylene blue solution was divided into 10 beakers. Weighed activated carbon samples were transferred to 9 beakers. The remaining 1 beaker was left as a blank with no activated carbon content. The blank sample was prepared to determine the self-decomposition of the methylene blue in daylight. The blank sample and 9 beakers were mixed at 160 rpm in WiseShake SHO-1D device for 1, 1.5, 2, 3, 4 and 12 h, impregnated and absorbance values were measured separately. The beakers were closed with parafilm to avoid any loss during the mixing process.

### 2.4. Characterization

#### 2.4.1. Scanning electron microscope analysis

The analysis was conducted in a COXEM Nicolet IS10 EM-30 brand scanning electron microscope (SEM) device to observe the surface morphology of the activated carbons produced in the experiment and the commercially available coconut shell activated carbon.

#### 2.4.2. X-ray photoelectron spectroscopy analysis

The analysis was conducted with a Thermo Scientific Al K-Alpha brand X-ray photoelectron spectroscopy device (XPS). Elemental and chemical analyses were conducted on the data collected at a depth of 10 nm of the experimental activated carbon and commercial activated carbon samples.

#### 2.4.3. Fourier-transform infrared spectroscopy analysis

The analysis was conducted with a Thermo Scientific NICOLET iS10 brand device on the experimental activated carbon and commercial activated carbon samples.

## 3. Results and discussion

### 3.1. SEM analyses

Surface morphology (SEM) images of the walnut shell, olive seeds and pomace activated carbon and commercial activated carbon samples are presented in Fig. 1.

It was reported that surface morphology is a significant adsorption parameter. It was determined that surface morphology was affected by parameters such as concentration, pH, viscosity, and carbonization. In the SEM photograph presented in Fig. 1, several micro and deep pores could be observed on the walnut shell. In pomace images,

deep and less porous structures were observed. Both micro and macro pores were observed on olive seeds, similar to the walnut shell. Micro pores were observed on the commercial activated carbon sample. It could be suggested that the porous structure had a positive effect on the adsorption capacity and removal of methylene blue. The best morphological structure was observed on walnut shell surface.

### 3.2. Fourier-transform infrared spectroscopy analyses

Surface functional groups are important in the adsorption process. Functional groups were determined with Fourier-transform infrared spectroscopy (FTIR) analysis. The peaks formed at 1,400; 2,983; 2,885; 2,103; 1,397; 3,661; 2,987; 2,898; 1,393; 1,058; 881, 600–700 $cm^{-1}$ belonged to various functional groups including alcohols, ketones, carboxyl groups and aromatic bonds (Fig. 2).

### 3.3. XPS analyses

In the elemental analysis, C, O, Si, Ca, K elements were determined and the element rates are presented in Annex-Table 1. Carbon activation leads to the release of volatile organic compounds from the structure, and a carbon-rich and highly stable product [11]. As seen in the tables, the highest carbon content following the commercial activated carbon sample was in the olive seed activated carbon product.

### 3.4. Adsorption

The absorbances of the activated carbon samples were measured to determine the rate of removal in the 10 mg/L methylene blue solution. The absorbance at 200–900 nm wavelengths were measured with the spectrophotometer.

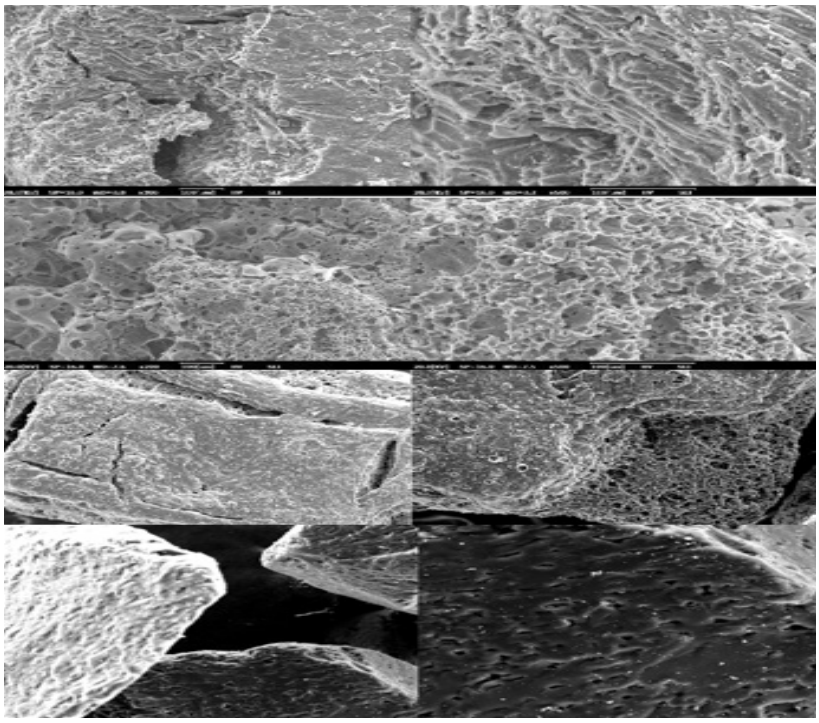

Fig. 1. Surface morphology in activated carbons.

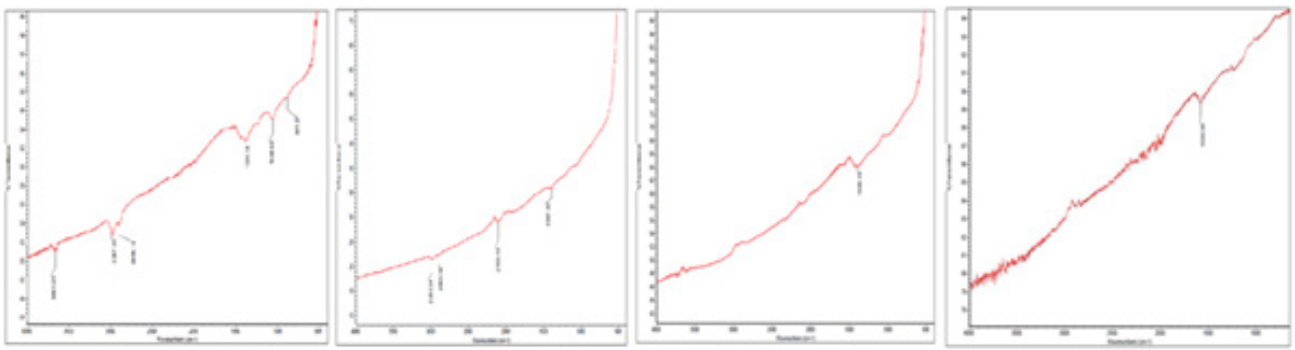

Fig. 2. FTIR images of walnut shell, olive pomace, olive seeds and commercial activated carbon, respectively.

Table 1
Spectrophotometric yields

| Type of material | Activated carbon weight (g) | Input absorbance (10 mg/L methylene blue) | Output absorbance (10 mg/L methylene blue) | Methylene blue removal (%) (*R*) |
|---|---|---|---|---|
| Walnut shell | 0.1 | 2.078 | 1.749 | 15.83 |
| Walnut shell | 0.3 | 2.078 | 1.549 | 25.45 |
| Walnut shell | 0.5 | 2.078 | 1.284 | 38.70 |
| Pomace | 0.1 | 2.078 | 1.341 | 35.46 |
| Pomace | 0.3 | 2.078 | 0.576 | 72.28 |
| Pomace | 0.5 | 2.078 | 0.270 | 89.41 |
| Olive seed | 0.1 | 2.078 | 1.029 | 50.48 |
| Olive seed | 0.3 | 2.078 | 0.331 | 84.07 |
| Olive seed | 0.5 | 2.078 | 0.151 | 92.73 |
| Blank | | 2.078 | 2.128 | 1.53 |
| Commercial activated carbon | 0.1 | 2.078 | 0.000 | 100.00 |
| Commercial activated carbon | 0.3 | 2.078 | 0.004 | 99.81 |
| Commercial activated carbon | 0.5 | 2.078 | 0.022 | 98.98 |

*Note*: Absorbance measured after 4 h at 663 nm.

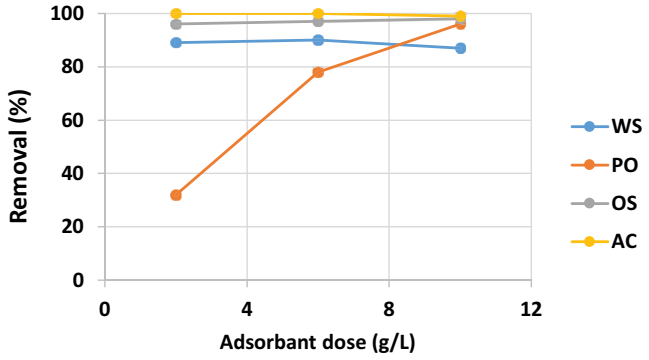


Fig. 3. Effect of adsorbent dose on decolorization.

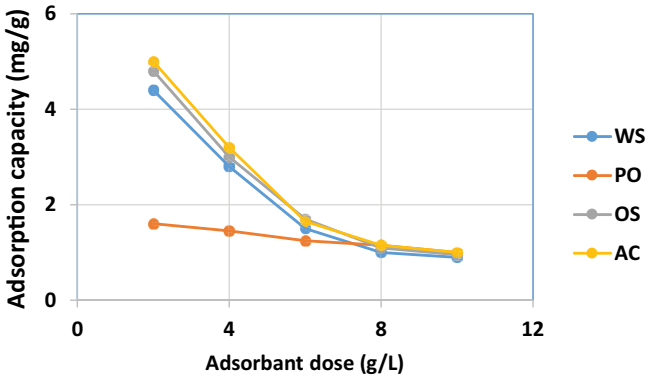


Fig. 4. Effect of adsorbent dose on adsorption capacity.

The maximum methylene blue absorbance was measured at 663 nm wavelength. The removal efficiency of the produced activated carbons was calculated with the Eq. (1). The yields based on spectrophotometer measurements are presented in Table 1.

As seen in Eq. (1) and Table 1, the best removal efficiency was observed in to the 0.5 g/50 mL olive seed activated carbon (92.73%) following the commercial activated carbon.

### 3.5. Impact of the adsorbent dose

The adsorbent dose is an important parameter for adsorption capacity. Figs. 3 and 4 demonstrate the effect of adsorbent dose of commercial activated carbon and experimental activated carbons on 10 mg/L methylene blue solution decolorization (*R*) and adsorption capacity (*Q*).

$$\text{Removal of dye}\left(R\right)=\frac{\left(C_o-C_t\right)}{C_o}\times 100 \quad (1)$$

$$\text{Adsorption capacity}\left(Q\right)=\frac{\left(C_o-C_t\right)V}{m} \quad (2)$$

where $C_o$ depicts influent concentration (mg/L), $C_t$ is the post-adsorption concentration (mg/L), $V$ is the volume (mL), and $m$ reflects the adsorbent mass (g). Adsorption was determined for 10 mg/L methylene blue solution. The effect of adsorbent dose on decolorization and adsorption capacity are presented in Figs. 3 and 4. As seen in Fig. 3, the yield increased with the increase in adsorbent dose in olive pomace and olive seed activated carbons, while in walnut shell activated carbon, the yield increased up to a certain dose and then decreased. It was observed that the dose increase in commercial activated carbon did not affect the yield significantly.

#### 3.5.1. Effect of time

Based on the absorbance measurements conducted with the spectrophotometer, it was determined that the highest removal yield was observed with the 0.5 g/50 mL olive seed activated carbon. In the time dependent experiment, the activated carbon with the highest removal efficiency was employed. The previously prepared 0.5, 5 and 10 mg/L methylene blue solutions were placed in 50 mL

beakers and 0.5 g olive seed activated carbon was added. Samples were removed with a syringe every hour and mixed at 160 rpm in a WiseShake device for 4 h and their absorbance was measured with a spectrophotometer. Adsorption capacities are presented in Fig. 5 based on the absorbent values. In the graph, it could be observed that although there were occasional small reductions in the adsorption capacity over time, the variations were not significant.

#### 3.5.2. Effect of dye concentration

In this experiment conducted with 0.5 g/50 mL olive seed activated carbon with the best removal efficiency, the adsorption capacities were calculated by increasing the methylene blue concentration. Measurements were conducted for 4 h. Adsorption capacities and concentration-dependent dye removal efficiencies are presented in Figs. 6 and 7. The increase in dye concentration led to an increase in adsorption capacity, and the dye removal efficiency increased up to a certain concentration and then fluctuated.

### 3.6. Adsorption isotherms

Adsorption isotherms are required to determine adsorbent surface properties, adsorption capacity and to explain the adsorption mechanism. It also describes how the adsorbent interacts with the pollution. The most common adsorption models are the Langmuir and Freundlich isotherms. Langmuir and Freundlich isotherms were applied to olive seed, walnut shell and pomace activated carbon samples.

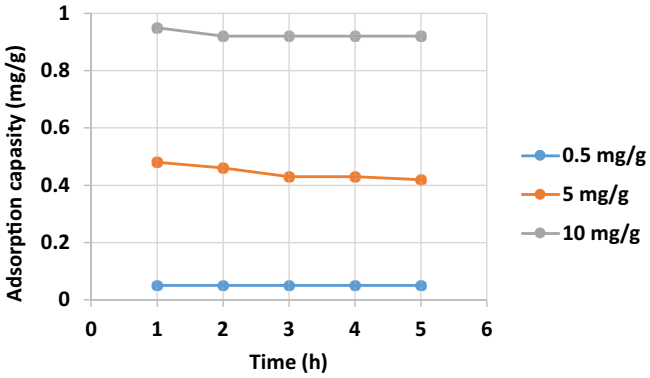


Fig. 5. Effect of time on adsorption capacity.

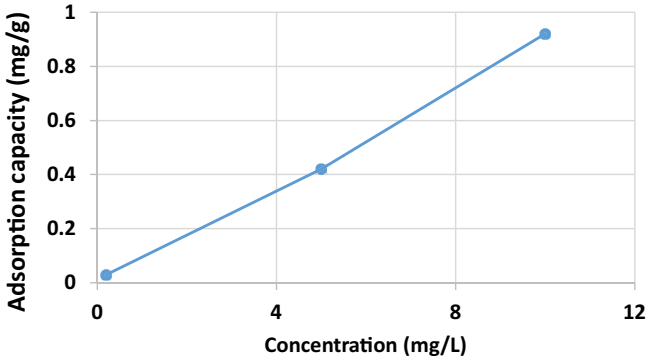


Fig. 6. Dye concentration-dependent variations in $Q$.

The Langmuir model describes the monolayer adsorption of dye molecules on a homogeneous surface, as indicated in Eq. (3).

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e \tag{3}$$

where $C_e$ is the dye concentration after adsorption (mg/L), $q_e$ depicts the solid phase concentration of the dye (mg/g), $K_L$ (L/g) and $a_L$ (L/mg) are the Langmuir constants.

The Freundlich isotherm, however, describes the non-uniform distribution on heterogeneous surface as presented in Eq. (4):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where $K_F$ reflects the adsorption capacity (L/g) at unit concentration and $1/n$ depicts adsorption density.

The activated carbon produced with the walnut shell changed the color of the solution after the adsorption, which led to different absorbance values measured with the spectrophotometer. Thus, it could not fully adapt to the Langmuir isotherm. Activated carbons produced with pomace and olive seeds fully adapted to the Langmuir isotherm and $R^2$ was very close to 1.

It was observed that activated carbons produced with olive seeds and pomace, which accommodated the Langmuir isotherm, adapted to the Freundlich isotherm as well. It was observed that the activated carbons produced with walnut shells changed the color of the solution after adsorption and could not adapt to the Freundlich isotherm. Langmuir model was drawn as $C_e/q_e$–$C_e$, and Freundlich model was drawn as $\log(q_e)$–$\log(C_e)$. The $R^2$ values for the Freundlich and Langmuir isotherms of the activated carbons are presented in Table 2. The Langmuir and Freundlich isotherm parameters for the active carbons produced with pomace that yielded a $R^2$ closest to 1 for both isotherms are presented in Table 2. Isotherm parameters for pomace are presented in Table 3. Moisture, ash, calorie and oil-grease rates for the adsorbent materials are presented in Table 4.

In the literature, the equilibrium data generally accommodated the Langmuir isotherm model. Yildiz [12] activated walnut shell with various acids and the activated walnut shells significantly improved the removal of MB. Adsorption of MB onto activated walnut shells accommodated the

Table 2
Isotherm $R^2$'s for activated carbons

| Type of material | Langmuir isotherm ($R^2$) | Freundlich isotherm ($R^2$) |
|---|---|---|
| Olive seed | 0.9533 | 0.8803 |
| Pomace | 0.9948 | 0.9995 |
| Walnut shell | 0.5302 | 0.3081 |

Table 3
Pomace isotherm parameters

| Type of material | Isotherm model | Parameter | Value |
|---|---|---|---|
| Pomace | Langmuir isotherm | $K_L$ (L/g) | 6.59 |
| | | $a_L$ (L/mg) | 4.1 |
| | | $Q_{max}$ (mg/g) | 0.92 |
| | Freundlich isotherm | $n_F$ | 5.53 |
| | | $K_F$ | 1.1115 |

Table 4
Sample moisture, ash, calorie and oil-grease rates

| Type of material | Moisture (%) | Ash (%) | Calorie (cal/g) | Oil-grease (%) |
|---|---|---|---|---|
| Walnut shell | 8.19 | 0.77 | 4435 | 1.185 |
| Pomace | 1.35 | 2.53 | 5128 | 8.198 |
| Olive seed | 0.82 | 2.19 | 5126 | 10.68 |

Langmuir adsorption isotherm. Adsorption capacity of WS, WS by hydrochloric acid, WS by sulfuric acid and WS by phosphoric acid were 9.7, 20.0, 19.6 and 38.5 mg/g, respectively. Similarly, Uddin and Nasar [8] employed the walnut shell as adsorbent and increasing the pH led to an increase in dye adsorption, and the adsorption mechanism functioned via the electrostatic attraction between negative adsorbent surface and positive dye molecules. The equilibrium data suited the Langmuir isotherm model, while the adsorption application was consistent with the pseudo-second-order kinetic model. Higher temperature reduced the adsorption of dye molecules. They determined that the optimum temperature was 30°C.

### 3.7. Adsorption kinetics

In Fig. 8, the methylene blue adsorption yield from the carbonized olive seed solution obtained with thermal treatment is presented based on time. The experiments conducted with 3 different sample volumes (2–10 g/L) revealed that the adsorption mechanism was gradual for up to 4 h. The adsorption mechanism was similar in all 3 volumes. In the experiments, although the adsorption rate decreased after 4 h, the yield was above 80%. In the experiment conducted with 10 g/L, it was observed that the yield remained stable (>92.73%) and reached an equilibrium after 4 h.

The adsorption efficiency of carbonized pomace based on time is presented in Fig. 9. It was observed that the data were similar to the olive seed data, and the yield reached 90% with 10 g/L.

The experiments conducted with 3 volumes (2–6-10 g/L) of carbonized walnut shell revealed that the adsorption mechanism was gradual for up to 4 h as presented in Fig. 10. It was observed that the adsorption rate decreased after 4 h. After 12 h, the adsorption efficiency was at 50%. It could be suggested that this could be due to the limitation of the walnut shell surface area during the carbonization stage.

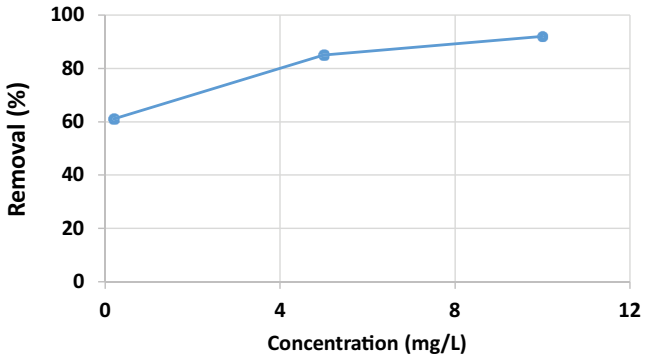


Fig. 7. Impact of dye concentration on removal yield.

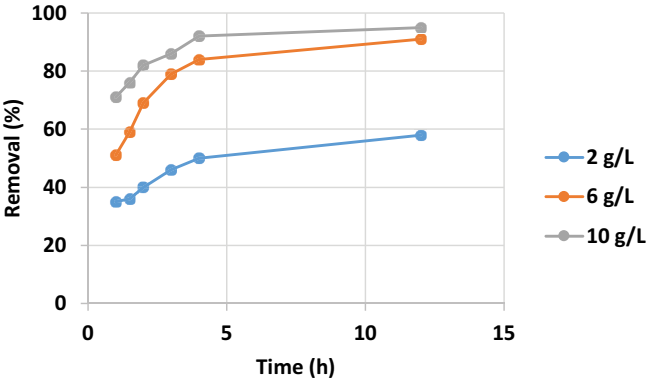


Fig. 8. Carbonized olive seed adsorption kinetics.

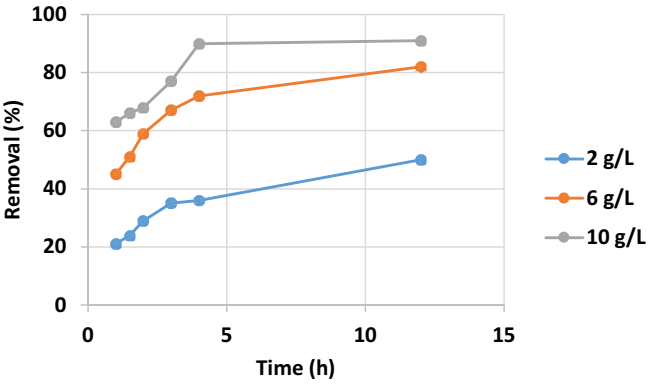


Fig. 9. Carbonized pomace adsorption kinetics.

The comparison of the adsorption performance of the carbonized materials (6 g/L) obtained with thermal treatment and commercial powder activated carbon is presented in Fig. 11. It could be suggested that 95% efficiency obtained within a short time such as 1 h with powder activated carbon with a particle size of 100 μm was due to the high surface area. On the other hand, over 80% adsorption efficiency was obtained with carbonized olive seed and pomace samples (1–4 mm grain range).

In other studies, it was determined that adsorption capacity of activated food waste was also high. Lu et al. [7], reported that methylene blue and Congo red dye

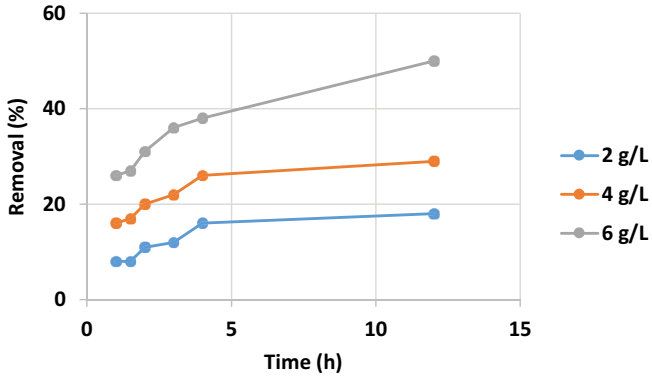


Fig. 10. Carbonized walnut shell adsorption kinetics.

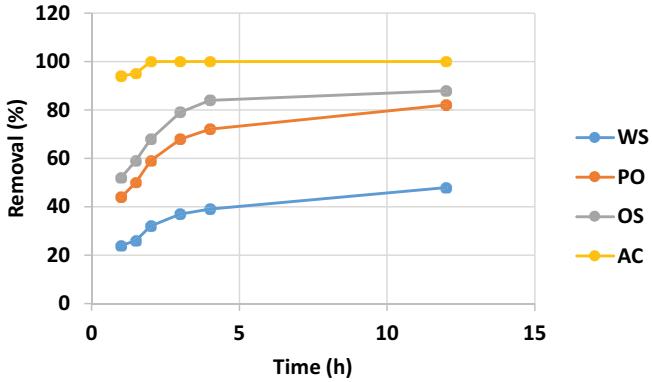


Fig. 11. Comparison of carbonized material with powder activated carbon.

adsorption capacity of walnut shell activated carbon varied between 314 and 400 mg/g for methylene blue and 281 and 443 mg/g for Congo red. Jahanban-Esfahlan et al. [13] argued that walnut shell could be employed for the removal of heavy metals, dyestuffs and pharmaceuticals. In another study adsorption potential of chemically activated olive pomace boiler ash (A-OPBA) for aqueous acid blue (AB 29) and methylene blue (MB) solutions was investigated. The kinetic and equilibrium adsorption experimental data was consistent with to the pseudo-second-order model and Langmuir isotherm. The maximum monolayer adsorption capacity of A-OPBA was 38.48 mg/g in 30°C and 149.11 mg/g for AB 29 and MB, respectively. The findings reported by Al-Ghouti and Sweleh [15] demonstrated that the maximum adsorption of methylene blue was observed at the pH value of 10. The maximum adsorption capacity of methylene blue was 714 and 769 mg/g with black and green activated carbon olive seeds, respectively. The maximum methylene blue removal efficiency was 79%. The equilibrium data best fitted to Freundlich isotherm ($R^2$ = 98%).

## 4. Conclusion

In the study, dye removal conducted with walnut shell, olive seed and pomace activated carbon samples produced in different times, concentrations and temperatures yielded the following findings:

SEM images of the optimum activated carbon samples were examined, and macro and micropores were observed on the activated carbon samples, and the best pore structure was in the olive seed activated carbon sample. The FTIR analysis demonstrated that alcohols, ketones and carboxyl groups formed in activated carbon samples. In the XPS analysis, C, O, Si, Ca, K were observed in activated carbon samples. The XPS findings demonstrated the highest C content was in the olive seed activated carbon sample after the commercial activated carbon. The activated carbon samples were employed to adsorb 10 mg/L methylene blue solution The adsorption experiment revealed that the best color removal was obtained with the olive seed activated carbon sample (92.73%) after the commercial activated carbon. The experiment conducted to determine the effect of the produced activated carbon and commercial activated carbon adsorbent doses on adsorption capacity and the water color removal efficiency demonstrated that the increase in the adsorbent dose improved the color removal efficiency in pomace and olive seed samples, while the efficiency increased up to a certain dose with walnut shell sample and then decreased, while the dose increase did not affect the efficiency with commercial carbon samples. The experiment findings demonstrated that the adsorption capacity decreased linearly with pomace, while the decrease was parabolic with walnut shell, olive seed and commercial activated carbon samples.

In addition to the chemical activation, physical activation method should also be employed in future studies to compare the findings obtained with both methods, and the most adequate method should be determined for the production of olive seed, pomace and walnut shell activated carbon samples.

## Declarations


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This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.


## Conflicts of interest/competing interests

Not applicable.

## Availability of data and material

All the necessary data have been mentioned in the paper. If other researchers need additional data, they can contact with the corresponding author.

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Annex-Table 1
XPS analysis results and elemental percentages of samples

| Sample | Name | Peak BE | FWHM eV | Area (P) CPS.eV | Weight % | *Q* |
|---|---|---|---|---|---|---|
| Olive seeds | K2p | 293.31 | 0.96 | 23,287.38 | 1.64 | 1 |
| | Cd3d | 400.34 | 1.49 | 10,430.46 | 0.36 | 1 |
| | C1s | 285.31 | 3.20 | 737,543.36 | 73.99 | 1 |
| | O1s | 532.23 | 3.68 | 327,708.64 | 18.12 | 1 |
| | Ca2p | 348.41 | 3.15 | 77,720.99 | 4.54 | 1 |
| | Si2p | 102.88 | 3.22 | 5,762.40 | 1.35 | 1 |
| Pomace | K2p | 293.43 | 1.42 | 57,538.84 | 3.88 | 1 |
| | C1s | 285.18 | 2.77 | 667,542.78 | 64.23 | 1 |
| | O1s | 532.22 | 3.07 | 438,855.05 | 23.27 | 1 |
| | Mg1s | 1,304.14 | 2.54 | 112,285.83 | 5.27 | 1 |
| | Si2p | 103.00 | 2.75 | 7,495.77 | 1.68 | 1 |
| | Al2p | 75.01 | 3.08 | 4,910.05 | 1.67 | 1 |
| Walnut shell | C1s | 285.16 | 2.75 | 496,736.44 | 56.49 | 1 |
| | O1s | 532.46 | 3.91 | 414,257.33 | 25.97 | 1 |
| | K2p | 294.32 | 4.43 | 173,304.72 | 13.82 | 1 |
| | Ca2p | 348.46 | 3.51 | 35,537.71 | 2.35 | 1 |
| | N1s | 396.48 | 3.67 | 16,045.97 | 1.37 | 1 |
| Commercial activated carbon | K2p | 293.19 | 2.03 | 26,519.06 | 1.80 | 1 |
| | C1s | 285.08 | 2.58 | 802,215.00 | 79.10 | 1 |
| | O1s | 532.26 | 4.27 | 243,119.74 | 13.27 | 1 |
| | Ag3d | 368.12 | 2.81 | 33,162.49 | 1.40 | 1 |
| | Na1s | 1,071.56 | 1.77 | 13,136.70 | 0.48 | 1 |
| | Ca2p | 349.17 | 7.10 | 35,310.18 | 2.00 | 1 |
| | Si2p | 102.32 | 2.39 | 3,568.05 | 0.85 | 1 |
| | Cl2p | 198.08 | 1.77 | 2,790.07 | 0.30 | 1 |
| | Zn2p | 1,022.75 | 2.32 | 12,117.50 | 0.40 | 1 |