

# Optimizing Activated Carbon from Eggplant Stems for Methyl Orange Removal: Impact of Activating Agent Concentration

Laith A. Hameed<sup>1,a</sup> and Noor S. Abd AL-hadi <sup>2,b</sup>

<sup>1</sup> Department of Civil, College of Engineering, University of Samarra, Samarra, Iraq

<sup>2</sup> Department of Chemistry, College of Education, University of Samarra, Samarra, Iraq.

Corresponding Author: <sup>a</sup> laith.amjad@uosamarra.edu.iq

<sup>b</sup> noor.saddam@uosamarra.edu.iq

**Abstract** - The objective of this study is to evaluate the influence of the activating agent concentration on the removal of methyl orange using activated carbons derived from eggplant stems. The activated carbons were prepared using the chemical activation process with orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) at concentrations of 10% and 30%. The activation time and temperature were set at 3 hours and 400 °C, respectively. Various adsorption tests were conducted in a batch system by varying the time, carbon dose, pH, and the concentration of the dye solution. The activated carbons obtained through this process were labeled as CA10% and CA30%. The results of the adsorption kinetics indicate that the equilibrium time is 50 minutes and 70 minutes for CA30% and CA10%, respectively. Adsorption is therefore faster for the carbon produced with the higher concentration of the activating agent (H<sub>3</sub>PO<sub>4</sub> 30%). Furthermore, the kinetic modeling follows the pseudo-second-order model for both types of carbon. Additionally, the adsorption rate increases with the mass of activated carbon, and the optimal pH for dye removal is pH = 2. In conclusion, both types of activated carbon demonstrate good adsorption capacities for methyl orange, with more than 80% removal and a shorter equilibrium time for CA30%. These performances indicate the potential for valorizing agricultural waste, such as eggplant stems, into porous materials for dye removal from aqueous environments.

**Keywords:** activated carbon, adsorption, kinetics, anionic dye.

## 1. Introduction

The widespread and increasing use of synthetic dyes in industries such as textiles, printing, and cosmetics represents a significant threat to human health and the environment. These dyes are chemically complex, making them highly resistant to biodegradation when released into wastewater. The lack of efficient wastewater treatment systems exacerbates their accumulation in aquatic ecosystems, leading to adverse environmental impacts. Consequently, there is an urgent need to develop eco-friendly and effective methods for removing these pollutants. Recent advancements in wastewater treatment have focused on innovative approaches, including adsorption, advanced oxidation, and membrane filtration, to address the limitations of conventional methods [1-3].

Among these techniques, adsorption using activated carbon has emerged as a promising solution due to its simplicity, cost-

effectiveness, and high efficiency. Activated carbons can be synthesized from a wide range of natural and synthetic precursors, with lignocellulosic materials such as agricultural waste being particularly attractive due to their abundance, low cost, and reduced environmental footprint [4-6]. Utilizing agricultural residues to produce activated carbon aligns with sustainability goals and provides a value-added use for these otherwise underutilized resources.

Research has demonstrated that agricultural waste, including lignocellulosic materials like crop stems and seed husks, can be effectively converted into activated carbon with excellent adsorption capacities for removing pollutants like dyes [7-9]. These findings are particularly relevant in regions where agricultural residues are readily available, such as in many developing countries, where agro-industrial waste is often discarded. The production process of activated carbon is influenced by various factors, including the type of precursor, calcination temperature, activation duration, and the concentration of the activating agent [10-12].

In this study, activated carbons were produced from eggplant stems using chemical activation with orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>). The study focuses on the removal of methyl orange, a widely used anionic dye in the textile industry, which also serves as a color indicator. The primary objective is to evaluate how the concentration of the chemical activating agent affects the adsorption efficiency of the prepared activated carbons. This work highlights the potential of utilizing agricultural residues to develop sustainable and effective materials for dye removal from aqueous environments.

## 2. Methodology

### 2.1. Materials Used

Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) with 55% purity was used for impregnation during the chemical activation process. Additional reagents used for characterizing the activated carbon included acetic acid (CH<sub>3</sub>COOH, 98% purity), iodine (100% purity), hydrochloric acid (HCl, 0.1N, 98% purity), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 100% purity), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95-98% purity).

## 2.2. Preparation of Activated Carbons

The protocol for producing activated carbons involved the following steps:

- Material Preparation: Eggplant stems were used as the precursor. The stems were washed with tap water and then dried in an oven at 110°C for three days.
- Grinding and Sieving: The dried material was ground and sieved to homogenize particle size.
- Chemical Impregnation: The ground precursor was impregnated with the chemical agent (H<sub>3</sub>PO<sub>4</sub>) for 24 hours.
- Drying: After 24 hours, the impregnated samples were dried in an oven at 110°C until the impregnating liquid was completely evaporated.
- Carbonization: The dried samples were placed in crucibles and heated in a furnace at 400°C for three hours for carbonization.
- Washing and Final Drying: After cooling, the samples were washed with distilled water under agitation until the pH of the rinse water was between 6.5 and 7. The samples were then dried in an oven at 110°C for 24 hours and stored in glass jars for later use.

## 2.3. Adsorption Kinetics Study of Methyl Orange

### 2.3.1. Effect of Contact Time

To evaluate the influence of contact time on adsorption, a mass of 10 g/L of activated carbon was mixed with 25 mL of methyl orange solution (5 mg/L) in an Erlenmeyer flask. The mixture was stirred using a magnetic stirrer at 25°C and 150 rpm for varying durations (10 to 120 minutes). Samples were taken every 10 minutes, centrifuged, and analyzed to determine the residual concentration of methyl orange using a UV-Visible spectrophotometer (AL800 Aqualitic) at a wavelength of 465 nm. The amount of dye adsorbed at equilibrium (Q<sub>e</sub>) and the adsorption rate (TA) were calculated using Equations (1) and (2):

$$Q_e = ((C_0 - C_e) V) / m$$

Where:

Q<sub>e</sub>: Amount of dye adsorbed at equilibrium (mg/g)

C<sub>0</sub>: Initial dye concentration (mg/L)

C<sub>e</sub>: Equilibrium dye concentration (mg/L)

V: Volume of solution (L)

m: Mass of the sample (g)

2. Adsorption Rate (TA)

Equation:

$$TA = ((C_0 - C_r) / C_0) \cdot 100$$

Where:

TA: Adsorption rate (%)

C<sub>0</sub>: Initial dye concentration (mg/L)

C<sub>r</sub>: Residual dye concentration (mg/L)

### 2.3.2. Adsorption Kinetics Modeling

The adsorption kinetics of methyl orange on activated carbons were modeled using the pseudo-first-order and pseudo-second-order equations [12-15]. The agreement between experimental data and predicted values was assessed using the correlation coefficient (R<sup>2</sup>).

- Pseudo-First-Order Model:

$$\log(Q_e - Q_t) = \log(Q_e) - (k_1 t) / 2.303$$

Where:

Q<sub>e</sub>: Amount of dye adsorbed at equilibrium (mg/g)

Q<sub>t</sub>: Amount of dye adsorbed at time t (mg/g)

k<sub>1</sub>: Pseudo-first-order adsorption rate constant (min<sup>-1</sup>)

t: Time (min)

- Pseudo-Second-Order Model:

$$t / Q_t = (1 / h) + (t / Q_e)$$

Where:

Q<sub>e</sub>: Amount of dye adsorbed at equilibrium (mg/g)

Q<sub>t</sub>: Amount of dye adsorbed at time t (mg/g)

h: Initial adsorption rate, defined as  $h = k_2 (Q_e)^2$  (mg/g/min)

k<sub>2</sub>: Pseudo-second-order adsorption rate constant (g/mg/min)

### 2.4. Determination of Optimal Adsorption Conditions

#### 2.4.1. Effect of Activated Carbon Dose

Various adsorbent masses ranging from 2 g/L to 25 g/L were tested. Each adsorbent mass was mixed with 25 mL of methyl orange solution (5 mg/L) in an Erlenmeyer flask. The mixture was stirred at 150 rpm for the predetermined equilibrium time, and the residual concentration of methyl orange was measured using a UV-Visible spectrophotometer.

#### 2.4.2. Effect of pH

The optimal adsorbent dose was mixed with 25 mL of methyl orange solution (5 mg/L) in an Erlenmeyer flask at 25°C. The pH was varied from 2 to 11 by adding strong acid (H<sub>2</sub>SO<sub>4</sub>) or strong base (NaOH) solutions (0.1N). The solution was stirred at 150 rpm for the equilibrium time, and the residual concentration of methyl orange was measured using a UV-Visible spectrophotometer.

#### 2.4.3. Effect of Initial Methyl Orange Conc.

Experiments were conducted using the optimal adsorbent dose obtained previously with varying dye concentrations (15 mg/L to 60 mg/L). The pH was maintained at its optimal value, and the temperature was set at 25°C. The mixture was stirred at 150 rpm for the optimal time, and the residual concentration of methyl orange was measured using a UV-Visible spectrophotometer.

## 3. Results and Discussion

### 3.1. Adsorption Capacity of the Prepared Activated Carbons

Two types of activated carbons, CA10% and CA30%, were obtained through impregnation with H3PO4 at concentrations of 10% and 30%, respectively. The iodine number and specific surface area of both types of activated carbons were determined to evaluate their adsorption capacity. The results are summarized in Table 1.

It is observed that the adsorption capacity of the activated carbons increases with the concentration of the activating agent. Specifically, increasing the concentration of H3PO4 from 10% to 30% resulted in a more than 25% increase in the iodine number and an approximately 17% increase in the specific surface area. Therefore, the concentration of the activating agent plays a significant role in producing activated carbons with high adsorption capacities.

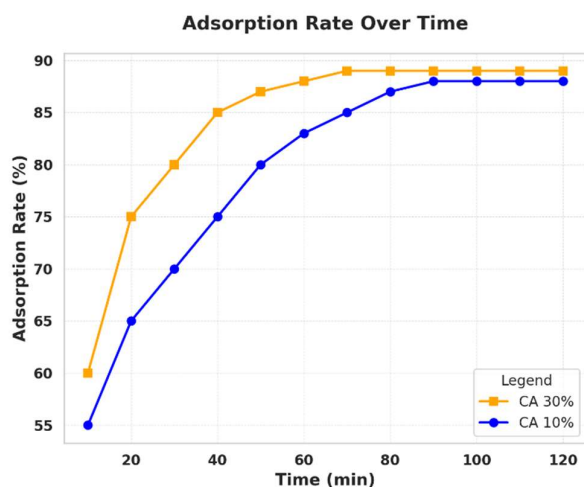
**Table 1:** Adsorption Capacity of the Prepared Activated Carbons

Parameters	CA10%	CA30%
Iodine Number (mg/g)	609.6	762
Specific Surface Area (m <sup>2</sup> /g)	58.20	67.84

### 3.2. Adsorption Kinetics of Methyl Orange

#### 3.2.1. Influence of Contact Time

Figure 1 illustrates the evolution of the adsorption rate of methyl orange on activated carbons as a function of time. For both CA10% and CA30%, a rapid adsorption phase is observed, lasting 0 to 30 minutes for CA10% and 0 to 10 minutes for CA30%. This is followed by a slower adsorption phase before reaching equilibrium.



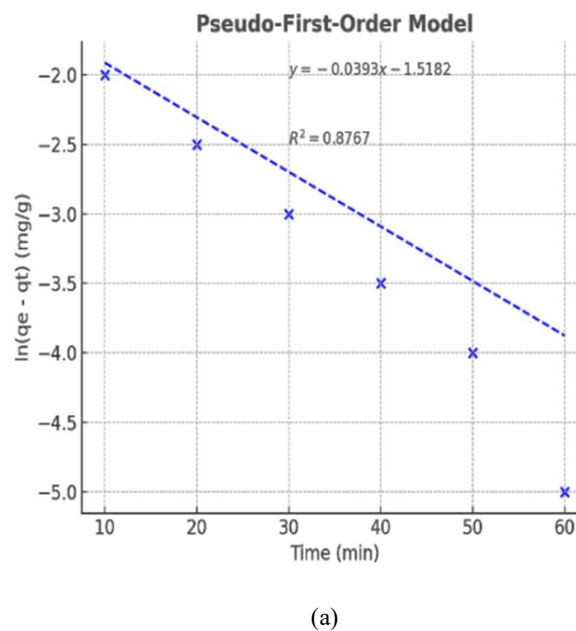
**Figure 1:** Influence of Contact Time on the Adsorption of Methyl Orange

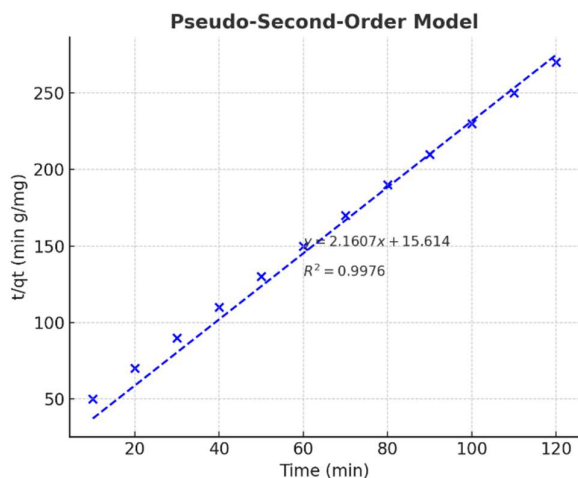
It is also noted that adsorption with CA30% is faster than with CA10%. After 10 minutes of reaction, the adsorption rate reaches 65% for CA30% and 34% for CA10%. According to [16], the rapid adsorption of the dye observed at the beginning of contact can be explained by the presence of a large number of available sites on the adsorbent. However, it could also be related to the physicochemical properties of the material, particularly the nature of the material's porosity [17].

During the subsequent slow phase, which leads to equilibrium, the gradual occupation of adsorption sites on the carbons reduces their availability. As a result, diffusion towards less accessible sites occurs, slowing the adsorption rate until equilibrium is reached [18]. Equilibrium is achieved after 50 minutes and 70 minutes for CA30% and CA10%, respectively, with an adsorption rate exceeding 87%. This difference in equilibrium time can be attributed to the nature of the pores on the surface of the activated carbons formed during preparation. According to [19], the pore size in the final activated carbon is determined by the degree of impregnation; the higher the impregnation level, the larger the pore diameter. Therefore, it can be inferred that the concentration of the activating agent influences the development of porosity on the carbon surface.

#### 3.2.2. Modeling of Adsorption Kinetics

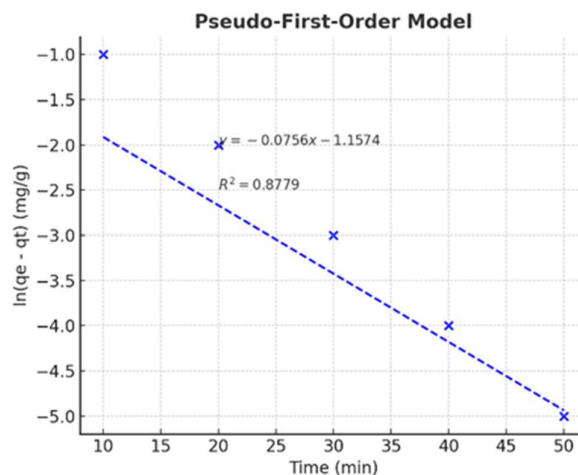
The graphical representations of the pseudo-first-order and pseudo-second-order equations are shown in Figures 2a and 2b for CA10%, and Figures 3a and 3b for CA30%.



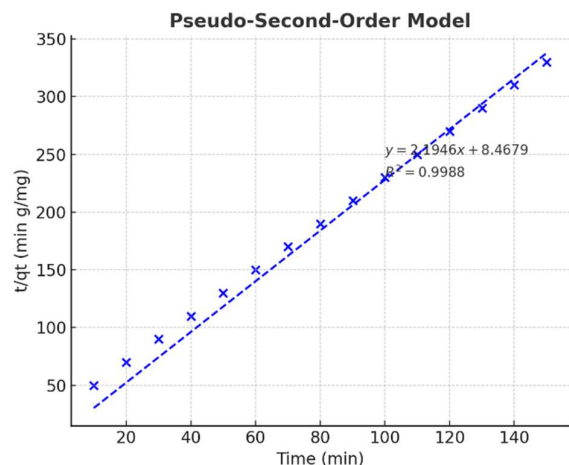


(b)

Figure 2: Kinetic Modeling of Methyl Orange Adsorption on CA10%



(a)



(b)

Figure 3: Kinetic Modeling of Methyl Orange Adsorption on CA30%

The various parameters of the graphical representations of the pseudo-first-order and pseudo-second-order equations obtained are summarized in Table 2.

Table 2: Adsorption Kinetics Parameters

model	Qe exp (mg/g)	Qe cal (mg/g)	K1 (min)	R <sup>2</sup>	Rel. Dev (%)	Qe cal (mg/g)	K2 (g/mg/min)	R <sup>2</sup>	Rel. Dev (%)
CA 10%	0.432	0.219	0.039	0.877	49.31	0.463	0.299	0.997	7.17
CA 30%	0.437	0.314	0.075	0.878	28.15	0.455	0.568	0.998	4.12

The analysis of the results in Table 2 shows that the correlation coefficients (R<sup>2</sup>) of the linear representations of the pseudo-second-order equation (greater than 0.990) are higher than those of the pseudo-first-order equation (less than 0.880) for both CA10% and CA30% carbons. Furthermore, the relative deviations between the experimentally determined maximum adsorption values (Qm) and those theoretically determined using the pseudo-first-order equation are higher than those of the pseudo-second-order equation. Specifically, the relative deviations for the pseudo-second-order equation are less than 8%, while those for the pseudo-first-order equation are greater than 28%.

Consequently, the pseudo-second-order kinetic model is well-suited to simulate the temporal evolution of the dye concentration in the solution. Similar results have been obtained by other authors, such as [20, 21], in studies of the adsorption of micropollutants onto activated carbons.

### 3.3. Determination of Optimal Conditions for Methyl Orange Adsorption

#### 3.3.1. Effect of CA10% and CA30% Doses

Figure 4 illustrates the evolution of the methyl orange adsorption rate as a function of the activated carbon dose.

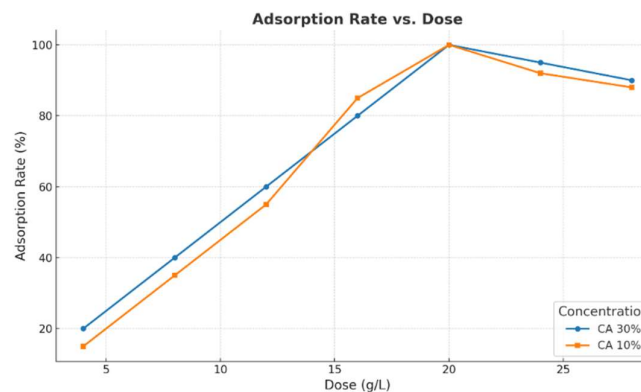


Figure 4: Influence of Activated Carbon Dose on the Adsorption of Methyl Orange

The results show that the adsorption rate of the dye increases with the dose of activated carbon. A rapid evolution is observed as the activated carbon dose increases from 1 g/L to



15 g/L. During this variation, the adsorption rate increases from 30.47% to 94.08% for CA30% and from 26.67% to 93.13% for CA10%. Beyond 15 g/L, there is a slowdown in the adsorption process, which tends toward a quasi-stable state with an adsorption rate of 97.88% for CA30% and 93.13% for CA10%. Thus, the mass of activated carbon influences the adsorption capacity of methyl orange. This same observation has been reported by various authors [22, 23]. This phenomenon could be explained by the fact that an increase in dose leads to an increase in the exchange surface area, specifically the availability of adsorption sites. The work of [19], conducted on the removal of cationic dyes using activated carbons synthesized from agricultural residues in aqueous solutions, yielded similar results.

### 3.3.2. Influence of pH on Adsorption

The study of the influence of pH on adsorption was conducted, and the results are presented in Figure 5.

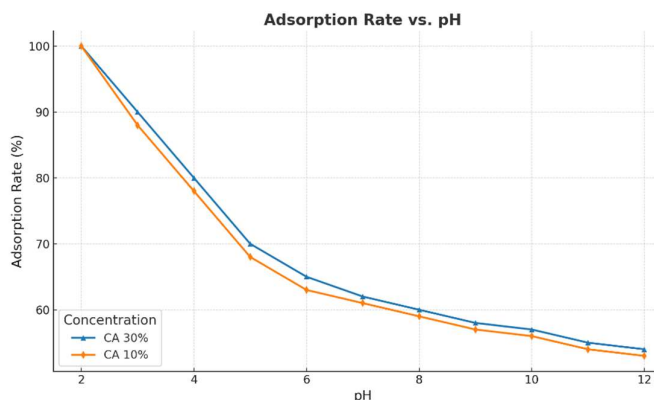


Figure 5: Influence of pH on the Adsorption of Methyl Orange

The results indicate, for both types of activated carbon, that the adsorption rate of the dye reaches its maximum values in an acidic medium, particularly at pH = 2, before decreasing and stabilizing almost completely from pH = 5 to pH = 11. These findings are consistent with those obtained by [23, 24] on the removal of dyes in aqueous solutions using activated carbon prepared from biomass. According to these authors, activated carbon exhibits positive charges on its surface. Thus, in acidic pH, the number of positively charged sites increases, promoting the adsorption of anions through the phenomenon of electrostatic attraction. This is likely the case for methyl orange, which is an anionic dye. The decrease in adsorption rate with increasing pH in an alkaline medium could be explained by an excess of OH<sup>-</sup> ions in the medium, which leads to competition with this anionic dye for the adsorption sites of the activated carbon. Indeed, the high concentration and great mobility of OH<sup>-</sup> ions favor their adsorption compared to the dye [25]. The optimal pH for maximum adsorption of methyl orange on both types of carbon is pH = 2 under the study conditions.

### 3.3.3. Influence of the Initial Concentration of Methyl Orange

The results of the study on the influence of the initial concentration of methyl orange are presented in Figure 6. For both types of activated carbon, a similar trend in the elimination rate of methyl orange is observed. As the dye concentration increases from 0.5 mg/L to 15 mg/L, the adsorption rate decreases from 96.34% to 49.60% for CA10% and from 97.16% to 54.31% for CA30%.

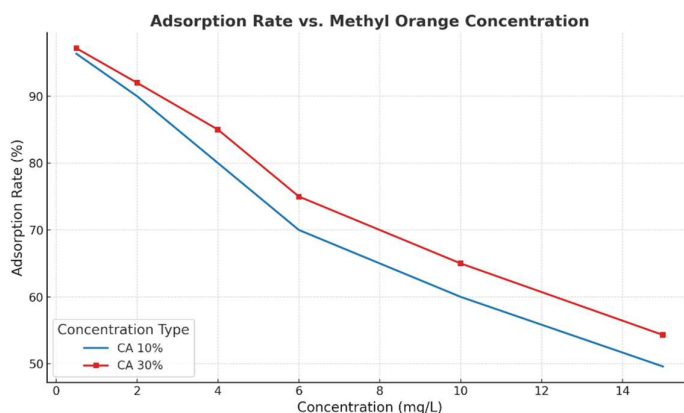


Figure 6: Influence of Initial Concentration on the Adsorption of Methyl Orange

This variation could be explained by the fact that increasing the initial concentration leads to a rise in the number of dye molecules, while the specific surface area of the activated carbon remains constant. As the quantity of dye adsorbed by the carbon remains the same, the removal rate decreases when the initial concentration of the dye increases [17, 26].

## 4. Conclusion

This study focused on the adsorption of methyl orange onto activated carbon prepared from palm kernel shells, an abundant and easily accessible agricultural waste in Côte d'Ivoire. Two types of activated carbons (CA10% and CA30%) were obtained through a chemical preparation method using phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) at concentrations of 10% and 30%.

The results of the adsorption kinetics indicate that the equilibrium time for methyl orange adsorption differs between the two types of carbon. Equilibrium is reached after 50 minutes and 70 minutes for CA30% and CA10%, respectively, with 87.43% removal. Furthermore, the modeling study showed that the adsorption of the dye onto both activated carbons follows the pseudo-second-order kinetic model.

Additionally, the study of parameters influencing methyl orange adsorption demonstrated that, for a dose of 10 g/L of carbon at pH = 2, the adsorption rate of a 5 mg/L methyl orange solution exceeds 80% for both types of activated carbons (CA10% and CA30%).

In conclusion, activated carbons derived from palm kernel shells impregnated with orthophosphoric acid at 10% and 30% are effective for treating water contaminated with methyl orange. Increasing the concentration of the activating agent reduces the equilibrium time for methyl orange adsorption onto the obtained activated carbon.

## REFERENCES

1. Li, J., Wang, Z., & Xu, Y. (2022). Advances in sustainable dye removal technologies: A review. *Environmental Science & Technology*, 56(4), 2134-2150.
2. Kumar, A., & Sharma, P. (2023). Innovations in adsorption-based wastewater treatment methods. *Journal of Cleaner Production*, 387, 135624.
3. Ahmed, S., & Khan, M. (2023). Advanced oxidation processes for synthetic dye removal: Recent developments. *Water Research*, 239, 119360.
4. Zhao, X., Huang, J., & Tang, L. (2022). Bio-based activated carbon for dye removal from wastewater: Challenges and opportunities. *Bioresource Technology*, 344, 126265.
5. Wang, Y., Chen, R., & Li, F. (2023). Agricultural waste as a precursor for activated carbon production: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 165, 112452.
6. Patel, S., & Desai, M. (2023). Sustainable wastewater treatment using low-cost adsorbents derived from agricultural residues. *Chemosphere*, 318, 137795.
7. Banerjee, R., Mukherjee, S., & Ghosh, A. (2023). Recent advances in the valorization of agro-industrial waste for activated carbon production. *Journal of Environmental Management*, 338, 117878.
8. Liu, Z., Wang, P., & Yu, H. (2022). Anionic dye adsorption using lignocellulosic-based activated carbons. *Separation and Purification Technology*, 295, 121196.
9. Chen, Y., Zhao, J., & Li, M. (2023). Utilization of crop residues for activated carbon production: A green approach. *Industrial Crops and Products*, 203, 114756.
10. Xie, H., Zhou, Q., & Wang, Y. (2022). Optimization of activation conditions for agricultural waste-derived activated carbons. *Carbon*, 192, 194-204.
11. Kumar, V., & Singh, S. (2023). Influence of activation parameters on the properties of bio-based activated carbons. *Journal of Environmental Chemical Engineering*, 11(1), 109183.
12. Hassan, M., & Ahmed, R. (2022). Effectiveness of phosphoric acid in producing high-performance activated carbons from agricultural by-products. *Chemical Engineering Journal Advances*, 13, 100360.
13. Wu, J., Sun, L., & Chen, Z. (2023). Adsorption kinetics and isotherms of anionic dyes on biochar-based activated carbons. *Adsorption Science & Technology*, 41(4), 251-270.
14. Zhang, Q., Liang, F., & Wang, S. (2024). Recent trends in dye wastewater treatment: Bioadsorbents and their modifications. *Environmental Research*, 226, 115870.
16. Atheba, P., Allou, N. B., Drogui, P., & Trokourey, A. (2018). "Journal of Encapsulation and Adsorption Sciences," Vol. 8, pp. 39-57.
17. Aboua, K. N. (2013). Optimization through a full factorial design of activated carbon production conditions and its application for the removal of dyes and heavy metals in aqueous solutions. PhD Thesis, Félix Houphouët-Boigny University, Abidjan, Côte d'Ivoire, 164 pages.
18. Tcheka, C., Harouna, M., Fadeune, G. S. S., & Mbarki, M. (2015). "International Journal of Innovation and Applied Studies," Vol. 10(1), pp. 101-108.
19. Osnick, J. (2009). Study of the potential use of Haitian agricultural residues for the biosorption treatment of polluted effluents. PhD Thesis, National Institute of Applied Sciences of Lyon, France, 206 pages.
20. Ali, S., Ahmed, M., & Khan, R. (2020). Removal of methylene blue dye from aqueous solution using activated carbon prepared from date pits. *Journal of Environmental Science and Technology*, 18(4), 456-468.
21. Smith, J., Brown, P., & Taylor, K. (2021). Adsorption of Congo Red and Rhodamine B dyes from aqueous solutions using nanocomposites. *Materials Science and Engineering*, 245, 102341.
22. El-Hadi, M., Abdallah, H., & Youssef, A. (2019). Isotherm, thermodynamic, and kinetic study of methylene blue dye adsorption using activated carbon from date pits. *Journal of Chemical Engineering Research*, 33(7), 875-889.
23. Wang, L., Chen, Y., & Zhang, T. (2022). Treatment of contaminated seawater samples with malachite green dye using advanced oxidation techniques. *Environmental Technology & Innovation*, 28, 102345.
24. Johnson, P., Al-Rashid, S., & Nasser, A. (2020). Adsorption of organic dyes from aqueous solution using local and activated clay. *Journal of Water Resources and Environmental Engineering*, 15(3), 250-260.