



# Optimized Zeolite Adsorption for Reducing Organic Load in Olive Mill Wastewater: Kinetics & Isotherm Analyses

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## Abstract

Olive mill wastewater (OMW) is a major contaminant in olive-growing regions due to its high organic and solid content. Although rich in nutrients, OMW also contains significant levels of antibacterial and phytotoxic phenolic compounds that hinder biodegradation. In this study, fresh OMW from olive mills in northern Jordan was treated with zeolite to reduce its organic matter, monitored through chemical oxygen demand (COD) measurements. The effects of temperature, pH, and zeolite concentration on COD removal were analyzed, revealing that higher temperatures (25°C to 45°C) reduced adsorption efficiency, while optimal removal occurred at pH 4. Increasing zeolite concentration from 1 g L<sup>-1</sup> to 2 g L<sup>-1</sup> improved removal rates. Adsorption kinetics followed a pseudo-second-order model with a rate constant ( $k_2$ ) of 0.62 g. mg<sup>-1</sup> s<sup>-1</sup>. The Freundlich isotherm provided the best fit for the adsorption data, with constants  $K_F$  and  $n$  determined as 1.33 and 1.22, respectively, outperforming the Langmuir model.

**Paper type:** Research paper

**Keywords:** Olive mill wastewater, Zeolite, Adsorption, Kinetics, Isotherms.

**Citation:** Khasawneh, H., Al-Ananzeh, N., BaniHani, F., Al-Bodour, A., Dawagreh, A., and Al Jarrah, A. "Optimized Zeolite Adsorption for Reducing Organic Load In Olive Mill Wastewater: Kinetics & Isotherm Analyses", Jordanian Journal of Engineering and Chemical Industries, Vol. 8, No.1, pp: 74-84 (2025).

## Introduction

Olive mill wastewater (OMW), or zebbar, is generated during the extraction process of the oil from the olive fruit in the olive trees-growing countries. The olive oil is produced mainly in countries around the Mediterranean such as Italy, Greece and Spain in addition to North Africa and the Middle East [Al-Ananzeh et al., 2016]. The portion of the wastewater discharged from the mills is fresh water added during the process to facilitate extraction of the oil, and the rest exists in the olive fruit itself. The extraction mills are often small plants, family-owned, and scattered around the olive farms in large numbers. Their effluent usually has high solid content of inorganic and organic compounds, some of which can be considered as fertilizers for plants and some are not environmentally friendly. Many researchers conducted studies on characterization of the olive oil mills effluents; the main contents were almost the same, however, their levels were found to depend on the location and on the degree of fruit ripeness. Phosphorus, potassium, magnesium, calcium, sodium and chlorine are examples of the inorganic chemicals present. Among the organic compounds are polyalcohols, polyphenols, pentoses, tannins and lipids.

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Received 30 Mar 2024

Jordanian Journal of Engineering and Chemical Industries (JJECI), Vol.8, No.1, 2025, pp: 74-84.

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Revised: 24 Jun 2024

Accepted 16 Feb 2025.



The highest percentage of the organic compounds present are the phenolic compounds (PC), such as 1, 2-dihydroxybenzene, derivatives of benzoic acid, phenylacetic acid, phenylethanol and cinnamic acid and many more [Ntaikou et al., 2009, Amaman et al., 2018, Ramosa et al. 2013]. Those chemical compounds result in elevated values of the biological oxygen demand (BOD) and the chemical oxygen demand (COD) In some countries, OMW is discharged without any treatment over surrounded lands where it seeps and ends up being mixed with water bodies [Jarbouli et al., 2008]. Some of the organic compounds in the effluent, especially the phenolic, are considered toxic to microorganism, and therefore, result in prolonging the biodegradation process in addition to inhibition of plant germination in the area surrounding the mills. This type of pollution, besides its strong odor, has also a severe impact, due to both toxicity and oxygen depletion, on aquatic life, and potable water [Paredes et al. 1999, Rinaldi et al., 2003, Shakhathreh et al., 2015, Al Ananzeh, 2021, Bani-Melhem et al., 2023.]. Treatment of the olive mills effluent in the olive oil producing countries, prior to discharging, to reduce the levels of toxic organic compound, has become a necessity.

To reduce the concentration of organic matters that causes the elevation of both the COD and BOD values, and other solid materials accompanying the OMW, different treatment techniques, biological, physical and chemical, are being investigated and reported in the literature. Among the reported biological treatments are the aerobic activated sludge and anaerobic digestion [Sarika et al., 2005, Paraskeva et al. 2006, Akdemir et al. 2006, Tziotziou et al., 2007, Ammary, 2004]. In the latter, the solid waste generated is converted to methane gas by microorganisms in the absence of oxygen [Arvanitoyannis et al. 2007]. Among the physical techniques often used are dilution, filtration, centrifugation, reverse osmosis and coagoflocculation [Paraskeva et al., 2007, Dhaouadi et al. 2008, Akdemir, 2009]. Although using these techniques results in lowering the concentration of organic compounds, and consequently, the value of both the BOD and COD, but not to the extent of where OMW can be discharged into lakes and rivers or over agricultural land, therefore, further treatment is required. A combination of physical and chemical treatment is usually utilized to reduce the concentration level of toxins to the permissible limit. Adsorption has been widely investigated and reported as a second stage following one or more of the physical methods. It involves the adherence of the substance to be removed (adsorbate) into the surface of a solid material (adsorbent) [Santi et al. 2008, Martino et al. 2013, Zagklis et al., 2014 Yangui et al., 2017]. The use of such sequence techniques has been proved and reported to reduce the concentration of pollutants, in the OMW, to relatively low levels. Activated clay has been used, following sedimentation and filtration, and reported to further reduce the concentration of organic compounds specifically the phenolic [Guneysu et al., 2019]. Activated carbon exhibited good results in reducing the content of organic matters by 83% and phenol by 94% [Azzam et al., 2011]. Resins, macroporous polystyrene and aromatic polymer were also investigated in removing of phenolic compounds from OMW by adsorption [Yangui et al., 2017]. Titanium dioxide, a common chemical compound known for its stability and ability to adsorb metals like arsenic and cadmium, was used to treat OMW and demonstrated a strong capacity to reduce COD-causing substances. [Bsoul et al., 2019].

Natural zeolite was used in the treatment of wastewater to remove organic chemical substances that are the reason behind the high COD and BOD values. It is a crystalline aluminosilicate material, with low density, high porosity and variable ratio of aluminum to silicate. Due to its chemical and physical properties, it gained a wide range of applications such as adsorption, adsorption, catalysis, ion exchange and molecular sieves. In adsorption, it is used in wastewater treatment to adsorb positive ions and heavy toxic metals such as lead, nickel, zinc, cadmium, copper, chromium and cobalt [Dawagreh et al., 2017, Hong et al., 2019, Taamneh et al., 2017, Bao et al., 2013]. A study showed that using zeolite for olive mill wastewater treatment was less effective compared to hydroxyapatite. Zeolite achieved only a 75% reduction in phenolic compounds and a 43% reduction in chemical oxygen demand. The previous study was performed at temperatures of 25 °C and 40 °C. The effect of the pH of the mixture (6–12) and initial COD of 86 g L<sup>-1</sup> were evaluated on OMW treatment [Nouara et al. 2020]. In another study, where zeolite was purchased from the Mineralogical Society of America, the effect of the pH of the mixture (3–6) and initial COD of 40-220 g L<sup>-1</sup> were evaluated on OMW treatment [Anwar, 2014].

Fadwa et al. (2022) studied the treat of olive mill wastewater using magnetic nanoparticles combined with zeolite to remove phenolic compounds. The nanoparticles were prepared and characterized, then mixed or coated with zeolite to form a nanocomposite media. The optimal conditions for removing phenolic compounds were identified, achieving up to 80% removal efficiency. Additionally, using granular activated carbon functionalized with a metal-organic framework significantly improved removal efficiency to 91% . of phenolic compounds in olive mill wastewater. [Abu-Dalo, et al., 2023]. In this research OMW was treated by natural zeolite, from a local source in Jordan, at different experimental conditions such as; initial concentration of COD, initial loads of zeolite and time of contact. These conditions were not covered by others researches. This study focused on measuring COD as the main parameter of concern as a measured pollutant to the environment. Other studies focused on different parameters and conditions when evaluating the treatment process of OMW by zeolite. As listed above in the research by [Nouara et al., 2020] and [Anwar et al., 2014].

## 1 Materials and Methods

The Zeolite, mainly natural aluminum silicate, was obtained from the south of Jordan (Tal-Elrmah), grounded and sieved to different particle sizes. The standard Tyler screen analysis was applied for the sieving process. The particle size used in the adsorption process

was the one that passed mesh number 80 [Osick, 1982]. Solid was soaked in distilled water and then dried in an oven at 105 °C for 48 hours, followed by another round of burning at 340 °C for 24 hours in an electric Muffle furnace. This process was carried out to clean the zeolite particles of any attached impurities and thus resulted in a loss of a mass equivalent to 13% of its original weight. All chemicals were obtained from Sigma-Aldrich.

The primary physical treatment stage of OMW was as follow: The OMW was collected from the effluent of local olive mills in the north of Jordan during the oil extraction season. It was left to settle for about one week, filtered by cloth filter to remove relatively large particles of solid, left for few days to let the sedimentation process takes place, decanted and filtered. The clear solution was centrifuged by using a Pro-Analytical centrifuge (Centurion Scientific Ltd) for about 5 minutes at 5000 rpm. The final solution was stored in a refrigerator at about 4 °C for further use. For each experimental run, the initial COD of OMW was kept constant. The necessary amount of zeolite was added, and the pH was adjusted in a 50 mL Erlenmeyer flask. The mixture was then placed in a JISICO Water Bath shaker and agitated at 200 rpm for the required time. After each run, samples were centrifuged with a Pro-Analytical centrifuge (Centurion Scientific Ltd) to separate solids from the aqueous solution.

The initial COD of OMW was measured after the physical treatment. It was found to be 38,000 mg L<sup>-1</sup>. Prior to carrying out the adsorption process, the OMW was diluted to reduce the COD to 4000 mg L<sup>-1</sup>. The BOD and COD of the OMW was studied and reported by many researchers [Rusan, M. J. M., et al., 2007, El Hadrami, I., et al., 2013] In this study the adsorbent was added to vials contain 100 ml of physically-treated and diluted OMW with adjusted pH and fixed temperature. The temperature was held constant. At different time periods, treated samples were filtered to remove the solid adsorbent, and then 0.2 ml of that sample was withdrawn and injected in a vial containing potassium dichromate oxidizing agent. The reaction was left to take place in an incubator at a temperature of 150 °C for two hours. The COD was measured at different time periods and recorded until equilibrium, indicated by no change in the COD value, is achieved and found to be in the range of 15,000 to 135,000 mg L<sup>-1</sup> and 37000 to 318,000 mg L<sup>-1</sup>, respectively. The suspended solids (SS) found to be in the range of 6000 to 69,000 mg L<sup>-1</sup> and the pH in the range of 4.6 to 5.8 [Bettazzi et al., 2006, Robles et al., 2000]. A complete characterization of the OMW used in this study was reported in a previous study [Bsoul et al., 2019]. The COD was tested using a COD analyzer model MD 100 COD, zeroed with deionized water, and utilizes Lovibond VARIO COD tube test reagents to investigate the effect of the adsorbent (zeolite) concentration on the adsorption of the organic substances in the OMW, and consequently, on variation of the COD value, three different zeolite solutions with the concentration of were utilized (1.0, 1.5 and 2.0 g L<sup>-1</sup>). The initial COD value of the solution was kept the same (4000 mg L<sup>-1</sup>), the temperature and the pH values were kept constant throughout each experiment at 25 °C and 4.7, respectively. The experiments were run until equilibrium is achieved. To investigate the effect of pH on the adsorption capacity of zeolite, the value of pH was varied between 2 and 10 using solutions of 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH). The initial COD value was kept constant at 4000 mg L<sup>-1</sup>, and the temperature was held the same and constant at 25 °C via using a water bath equipped with a temperature controller (JISICO Water Bath).

The effect of temperature, in this study, was evaluated by using three different temperatures, 25, 35 and 45 °C and they were kept constant throughout the experiments by means of a water bath equipped with a temperature controller. The pH value was also kept constant at 4.7. In order to determine the reaction kinetic that best describes the experimental data obtained, different reaction orders were proposed and tested. The results (COD uptake versus time) were plotted using the linear form of each of those models.

The following reaction orders and rate laws were investigated:

(1) Lagergren's pseudo-first order rate equation. First proposed by Lagergren [Al Ananzeh, 2021a].

$$\ln(q_e - q_t) = \ln(q_e) - k_1 * t \quad (1)$$

where  $q_t$  (mg g<sup>-1</sup>) is the COD uptake at any time ( $t$ ),  $q_e$  (mg g<sup>-1</sup>) is the COD uptake at equilibrium, and  $k_1$  is pseudo-first order reaction constant.

(2) Pseudo-second order rate equation [Ho et al. 1999, Al-Ananzeh 2021b]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (2)$$

where  $h = k_2 q_e^2$  and  $k_2$  is constant of the pseudo-second-order kinetics rate model ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{s}^{-1}$ ).

The COD up take with time ( $q_t$ ) ( $\text{mg L}^{-1}$ ) per unit mass of zeolite can be calculated using the formula:

$$q_t = (C_o - C) * \frac{V_s}{m} \quad (3)$$

where  $C_o$  and  $C$  are the initial concentration of adsorbate and its concentration any time, respectively, in  $\text{mg L}^{-1}$ , whereas  $V_s$  (L) is the volume of sample and  $m$  (g) is the mass of sorbent. The COD uptake at equilibrium ( $q_e$ ) is calculated using the following formula:

$$q_e = (C_o - C_e) * \frac{V_s}{m} \quad (4)$$

where  $C_e$  is the COD value at equilibrium.

Adsorption isotherms are well known models often used to describe the relationship between the amount of adsorbate on the surface of adsorbent and its equilibrium concentration in the bulk phase at constant temperature. The experimental results normally generated are variation of concentration with the time. Freundlich and Langmuir models are among the most commonly utilized isotherms to model the experimental data of adsorption. Freundlich, an empirical model, initially proposed to predict the amount of gas adsorbed per unit mass of the adsorbent, is given in equation 5.

$$q_e = K_F \times C_e^{-n} \quad (5)$$

where  $q_e$  is the COD uptake per unit mass of the adsorbent (zeolite) at equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  is the COD value at equilibrium ( $\text{mg L}^{-1}$ ) in the solution,  $K_F$  and  $n$  are constants and they depend on the characteristics of adsorbent and adsorbate at certain temperature and also can manifest the adsorption capacity and intensity, respectively. The higher the value of  $K_F$  and the smaller the  $n$  value indicate higher uptake at equilibrium. Their values can be obtained from the slope and intercept of the line generated by plotting the linear adsorption isotherm form ( $\log q_e$  vs.  $\log C_e$ ) given in equation 6.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

The linear form of Langmuir isotherm is given in equation 7. This isotherm is a semi empirical model and was built based on certain assumptions; the active sites on the surface of the adsorbent are fixed, adsorbent molecules do not interact, the adsorbate form a single layer on the surface of the adsorbent and dynamic equilibrium is involved.

$$\frac{1}{q_e} = \frac{1}{Q_m} + \left( \frac{1}{C_e} \times \frac{1}{b \times Q_m} \right) \quad (7)$$

where  $Q_m$  and  $b$  are the coefficients of the isotherm.

Both isotherms, Freundlich and Langmuir, were tested to find out which model represents the best fit for the experimental results. The correlation coefficient ( $R^2$ ) was used to determine the validity of each model; higher value of  $R^2$ , indicates better representation of the data

## 2 Results & Discussion

### 2.1 Effect of Contact Time

Variation of the COD, in the solution, versus the contact time, for the three zeolite concentrations (1, 1.5 and 2  $\text{g L}^{-1}$ ), is depicted in **Figure 1**. The temperature (25 °C) and pH value (4.7) were held the same for the three-adsorbate concentrations throughout the experiments. The rate of adsorption was high at the beginning of the adsorption process; the COD dropped from 4000  $\text{mg L}^{-1}$  to 2270  $\text{mg L}^{-1}$  in a contact time period of 15 minutes for a zeolite concentration of 2.0  $\text{g L}^{-1}$ . However, the rate of adsorption, and consequently,

the COD uptake then experienced an insignificant change as the COD-time curve remained almost horizontal up to a contact time of 60 minutes. The curves representing the other two zeolite concentrations (1.5 and 1.0 g L<sup>-1</sup>) have exhibited similar behavior. The experiments were terminated, after one hour, and the equilibrium concentration, represented by no change in the COD value, were about 2200, 2310 and 2740 mg L<sup>-1</sup> for an initial COD of 4000 mg L<sup>-1</sup> and zeolite concentrations of 2.0, 1.5 and 1.0 g L<sup>-1</sup>, respectively. The initial high solute concentration, strong attraction of active groups for COD, and available empty sites on the solid surface cause strong surface binding. As time goes on, fewer adsorbent sites and a lower concentration gradient lead to a slower rate of COD adsorption onto the zeolite powder [ Al Ananzeh et al., 2023]

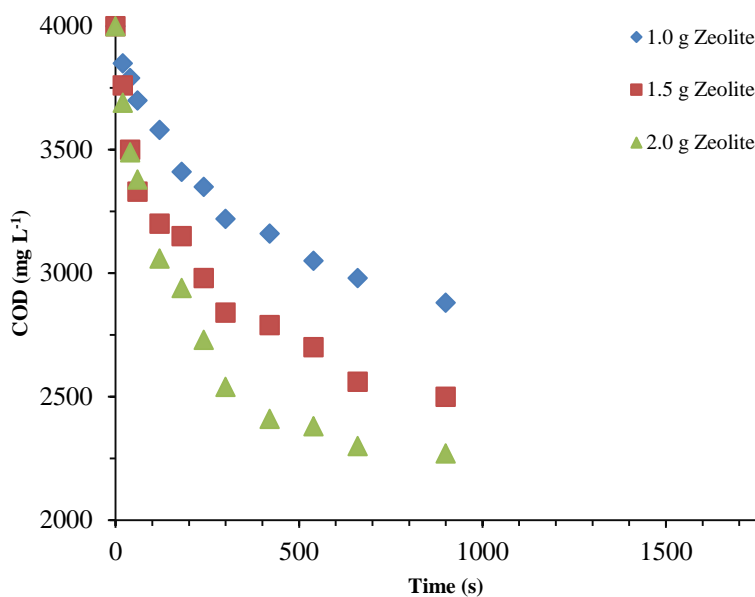


Fig. 1: Variation of COD with the adsorption time at different zeolite loading per liter.

### 2.2 Effect of Adsorbent Concentration

The effect of zeolite concentration was investigated through using three different values (2.0, 1.5 and 1.0 g L<sup>-1</sup>). The solution initial COD concentration was held the same at 4000 mg L<sup>-1</sup>, the temperature and pH value were both kept constant at 25 °C and 4.7, respectively. The initial COD uptake rate and COD uptake at equilibrium were found to be proportional with the amount of zeolite utilized as exhibited by Figure 2. The COD percent removal, at equilibrium, was found to be 31.5, 42 and 31.5% for zeolite concentration of 1.0, 1.5 and 2.0 g L<sup>-1</sup>, respectively. This improvement in COD removal is due to more active and empty adsorption sites being available as concentration of adsorbent was increased [Khader et al., 2021].

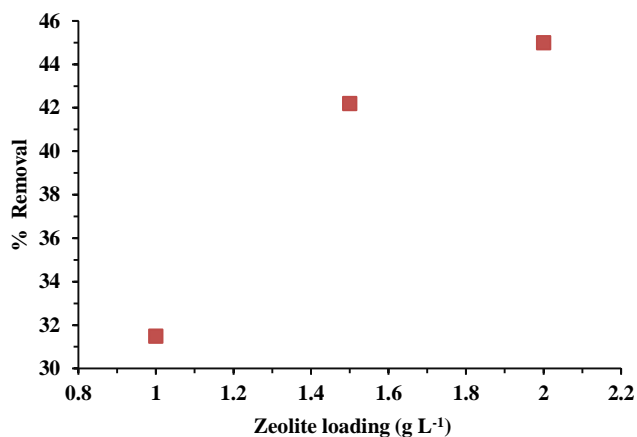
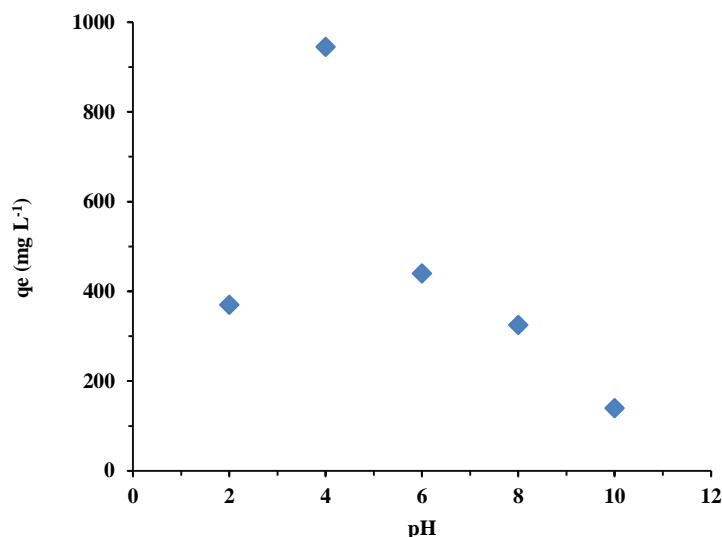


Fig. 2 : The COD-causing chemical removing percentage (% Removal) as a function of zeolite mass in solution.

### 2.3 Effect of pH

Effects of pH on adsorption of the matters that cause elevation of the COD value in the OMW by zeolite are depicted in **Figure 3**. Evidently, and as can be clearly seen, the COD uptake has increased and reached a maximum at a pH value of 4.7 then decreased. Therefore, the highest COD uptake ( $q_e$ ) corresponds to a pH value of 4.7. Reduction in adsorption, for pH values greater than 4.7, could be due to either some chemical reactions between the different chemical compounds in the OMW or the appearance of a new competitor for the adsorbate active sites. High pH levels can significantly impact the structure of zeolite, which in turn affects its efficiency in removing COD from wastewater. At high pH, the crystalline structure of zeolite can be altered. The increased alkalinity can cause the dissolution of the aluminosilicate framework, leading to a loss of structural integrity. This can reduce the number of active sites available for adsorption. The alteration in the zeolite structure can decrease its surface area and porosity. This reduction in surface area limits the zeolite's ability to adsorb organic pollutants, thereby lowering its COD removal efficiency [Lechert et al., 2023, Kordala et al., 2024]. Maintaining an optimal pH range is crucial for maximizing the efficiency of zeolite in COD removal processes.

Effects of pH on COD removal by zeolite have been studied and reported by different researchers. At low pH less than 3, the zeolite can become protonated, which can reduce its adsorption capacity. The presence of excess hydrogen ions can compete with organic molecules for adsorption sites, leading to lower COD removal [Detho et al., 2023]. At high pH levels, more than 9, a decrease in COD removal efficiency was obtained. This was related to change in structure of zeolite, reducing the number of active sites available for adsorption [Tetteh et al., 2020]



**Fig. 3** The COD uptake,  $q_t$  in (mg L<sup>-1</sup>) at different pH values.

## 2.4 Effect of temperature

The effect of temperature was evaluated by using three different temperatures, 25, 35 and 45 °C. The initial COD was kept the same (4000 mg L<sup>-1</sup>) and the pH value was also held the same (4.7) for the three experiments. **Figure 4** exhibits variation of the COD uptake with the time for the three temperatures utilized. The bonds usually formed between the adsorbent and adsorbate could be either physical or chemical, and consequently, the formation of these bonds can be profoundly affected by the temperature; increasing the temperature can accelerate the adherence of the adsorbate to the adsorbent surface if the reaction is endothermic and could reduce the removal rate if the reaction is exothermic. [Marczewski et al., 2016, Al-Ananzeh et al., 2023]. It's quite clear that the COD uptake is inversely proportional with the temperature for the same contact time. For the two temperatures (25 and 35 °C) the uptake was very close; however, it was much lower for the 45 °C. For example, for a contact time of 4 minutes the amount of the COD-causing chemical adsorbed were 635, 605 and 400 mg/g for the temperatures 25, 35 and 45 °C. This indicates that the adsorption could be classified as an exothermic reaction.

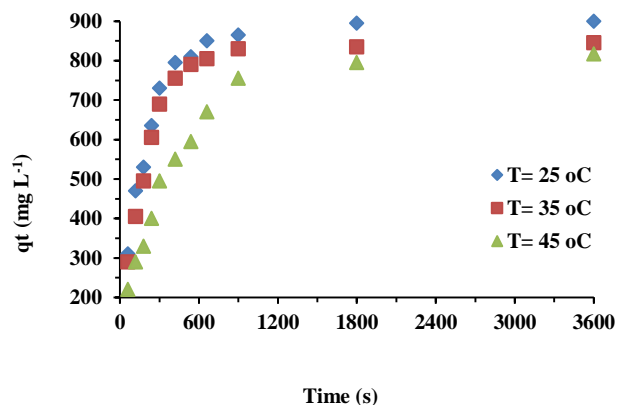


Fig. 4 Variation of the COD uptake ( $q_t$  ( $\text{mg L}^{-1}$ )) with the adsorption time at different temperatures

### 2.5 Kinetics Study and Adsorption Isotherms

To predict the mechanism of the adsorption process and find out the reaction rate law that provide the best representation of the data, the experimental data obtained were plotted using the Lagergren’s first order and pseudo second order rate laws, given by equations 1 and 2, respectively. **Figure 5** represents a graph of  $\ln (q_e - q_t)$  versus time (s) in part A for the pseudo first-order kinetics and  $t/q_t$  (s. g.  $\text{mg}^{-1}$ ) versus the time (s) in part B for the pseudo second order kinetics. The initial COD value was  $4000 \text{ mg L}^{-1}$ , the pH value was 4.7 and the temperature held at  $25 \text{ }^\circ\text{C}$ . It was quite evident that the best model to represent the experimental data was found to be the pseudo second order rate law; a straight line was obtained, with a correlation coefficient ( $R^2$ ) of over 0.99, while  $R^2$  for the pseudo first order was about 0.95, which indicates that it represents the best fit. The fitting to the pseudo-second-order model suggests that the adsorption process is likely controlled by chemisorption, requiring valence forces through sharing or exchange of electrons between adsorbent and adsorbate. A high correlation coefficient indicates that the pseudo-second-order model better describes the adsorption kinetics, implying that the rate of adsorption is more dependent on the availability of adsorption sites rather than the concentration of the adsorbate. The model often aligns with diffusion-controlled processes, where the rate-limiting step involves the movement of adsorbate molecules to the adsorption sites [Hube et al., 2019, Simonin 2016]. The high  $R^2$  value designates a more precise prediction of the adsorption behavior over time, which is vital for designing and optimizing adsorption systems. The slope of the line is 0.001 which represents  $1/q_e$ , and the intercept is 0.1157, which represents  $(1/k_2q_e)$ . Consequently, the reaction constant ( $k_2$ ) is calculated and found to be  $8.643 \times 10^{-6} \text{ g. mg}^{-1} \text{ s}^{-1}$ .

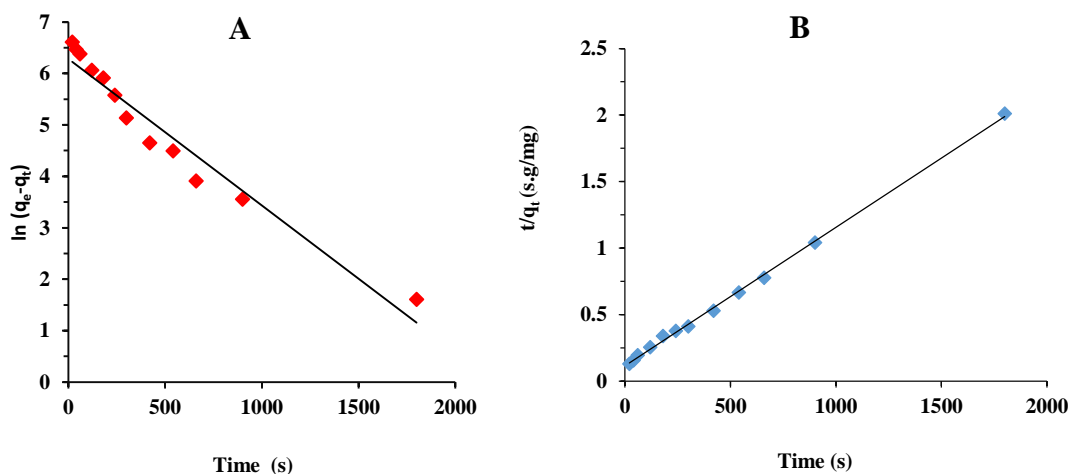
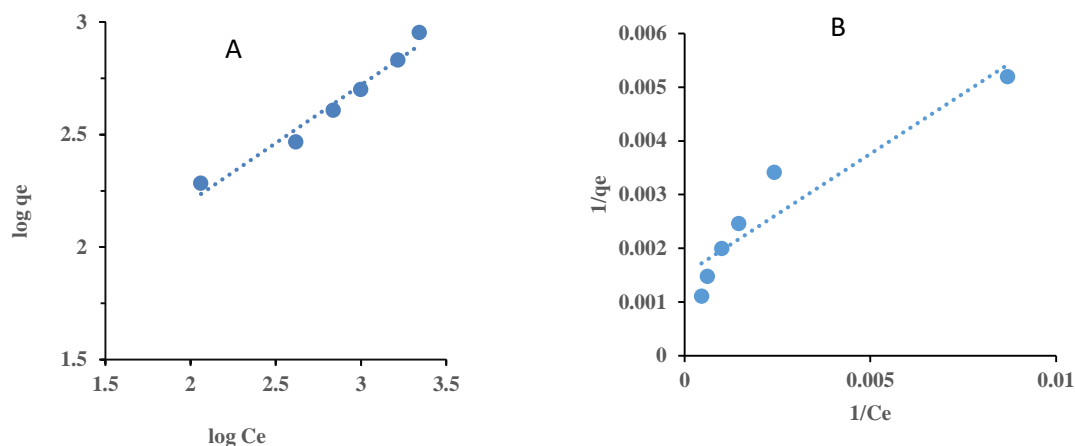


Fig. 5. Adsorption Kinetics at  $25 \text{ }^\circ\text{C}$ . A: Pseudo-first order, B-pseudo-second order.

To correlate the concentration of the COD-causing matters in the liquid phase and on the surface of zeolite, at equilibrium, Langmuir and Freundlich isotherms were both used to fit the experimental data obtained. **Figure 6** depicts fitting the data using the linear form of Freundlich isotherm;  $\log q_e$  was plotted versus  $\log C_e$  as shown in equation 6. The model exhibits a perfect fit; it was a much better fit than that exhibited by Langmuir isotherm. The coefficient of correlation ( $R^2$ ) is about 0.96. This  $R^2$  value recommends that the Freundlich model accurately describes the adsorption behavior of COD-causing matters on the zeolite surface. The isotherm constants  $K_F$  and  $n$  are calculated to be 14.88 and 1.937, respectively. A value of  $n$  between 1 and 10 shows favorable adsorption conditions. Here, the value proposes that the adsorption process is beneficial and effective. The constant  $K_F$  is linked to the adsorption capacity of the adsorbent. A high  $K_F$  value of 14.88 specifies a higher capacity of the zeolite to adsorb COD-causing matters. The Freundlich isotherm implies that the adsorption happens on a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. This means that different sites on the zeolite surface have different affinities for the COD-causing matters [Al-Ananzeh 2021, Vigdorowitsch et al., 2021, Al-Ananzeh et al., 2023, Kaiblinger et al., 2024]. Contrasting the Langmuir isotherm, which assumes monolayer adsorption on a surface with a finite number of identical sites, the Freundlich isotherm is empirical and does not assume a uniform surface or a single layer of adsorption. This makes it more flexible and often a better fit for real-world data where surface heterogeneity is present.



**Fig. 6.** Isotherms study results: A: Freundlich isotherm, B: Langmuir isotherm

## Conclusions

This study explored the ability of natural zeolite to adsorb and reduce organic compounds in olive mill wastewater (OMW). The results demonstrated that zeolite effectively reduced the chemical oxygen demand (COD) of OMW, with removal percentages ranging from 31.5% to 46.7%. The COD removal efficiency was inversely related to the initial concentrations, achieving the highest removal of approximately 47 % at an initial concentration of 4000 mg L<sup>-1</sup>. Additionally, COD uptake decreased with increasing temperature, as observed at 25 °C, 35 °C, and 45 °C, indicating an exothermic adsorption process. The maximum COD removal occurred at an optimal pH of 4.7.

Kinetic analysis revealed that the adsorption process followed a pseudo-second-order reaction rate model, supported by a high correlation coefficient ( $R^2 > 0.99$ ), compared to the pseudo-first-order model ( $R^2 \approx 0.95$ ), confirming its better fit and providing a more accurate representation of the experimental data. The pseudo-second-order model's better fit implies that the adsorption process is primarily controlled by chemisorption and diffusion mechanisms. The slope of the pseudo-second-order plot was 0.001, representing  $1/q_e$ , while the intercept was 0.1157, corresponding to  $(1/k_2q_e)$ . From these values, the reaction constant ( $k_2$ ) was calculated as  $8.643 \times 10^{-6} \text{ g} \cdot \text{mg}^{-1} \text{ s}^{-1}$ .

The Freundlich isotherm model provided a more accurate representation of the adsorption data compared to the Langmuir model, with a correlation coefficient ( $R^2$ ) of approximately 0.96, indicating a strong fit. The Freundlich constants  $K_F$  and  $n$  were determined to be 14.88 and 1.937, respectively. The Freundlich isotherm fit points to that the adsorption process is taking place on a heterogeneous surface with changing affinities, and the adsorption is favorable and efficient under the given conditions. Overall, the findings highlight the effectiveness of natural zeolite in reducing organic compounds in OMW through adsorption.



## Nomenclature

$V_s$	=	Volume of the sample	L
$m$	=	Mass of the adsorbent	g
$k_1$	=	Pseudo-first-order reaction constant	$s^{-1}$
$k_2$	=	Pseudo-second-order reaction constant	$g \cdot mg^{-1} s^{-1}$
$h$	=	Initial adsorption rate	$mg g^{-1} s^{-1}$
$K_F$	=	Freundlich isotherm constant	$mg g^{-1}$
$n$	=	Freundlich isotherm constant	[-]
$Q_m$	=	Langmuir isotherm constant	$mg g^{-1}$
$b$	=	Langmuir isotherm constant	$L mg^{-1}$
$R^2$	=	Coefficient of determination	[-]
pH	=	Measure of acidity or alkalinity	[-]
T	=	Temperature	$^{\circ}C$
rpm	=	Revolutions per minute	[-]
SS	=	Suspended Solids	$mg L^{-1}$
HCl	=	Hydrochloric acid	[-]
NaOH	=	Sodium hydroxide	[-]
NSP	=	Nanoscale Silica Particles	[-]
ZNP	=	Zeolite Clinoptilolite Nanoparticles	[-]
Clin	=	Clinoptilolite	[-]
PC	=	Phenolic Compounds	[-]
BOD/COD	=	Ratio used to assess the biodegradability of wastewater	[-]
Langmuir	=	Isotherm model for monolayer adsorption on a homogeneous surface	[-]
Freundlich	=	Isotherm model for adsorption on a heterogeneous surface	[-]
Pseudo-First-Order	=	Kinetic model for adsorption based on concentration difference	[-]
Pseudo-Second-Order	=	Kinetic model for adsorption based on square of concentration difference	[-]

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