

Article

Bioadsorbents for the Removal of Pollutants in Wastewater: Adsorption Kinetics, Validation Test Using Methylene Blue and Methyl Orange

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Abstract

The presence of emerging contaminants in water has led to a need for the development of new materials and treatments. Four low-cost adsorbents derived from lignocellulosic biomass waste (pine nut shells and olive stones) were prepared via chemical treatment (with H_3PO_4 or $NaOH$) followed by thermal activation (at 550 °C under N_2). Characterization of the bioadsorbents was carried out using N_2 adsorption–desorption isotherms, FTIR and Raman spectroscopic analyses, and pH_{pzc} determination. The electrostatic interactions between the adsorbent surface and the dyes were determined, and it was found that the interactions in both adsorbents were attractive for the methylene blue and repulsive for methyl orange, at pH basic or neutral. The performance of the obtained activated carbons was evaluated at lab scale with two dyes (methylene blue and methyl orange), and a comparison was made between both adsorbents and with commercial charcoal. The H_3PO_4 -activated adsorbents exhibited higher adsorption capacities (up to 300 mg/g for methylene blue and 285 mg/g for methyl orange), with adsorption efficiencies close to 100%. More than 10 adsorption–desorption cycles were performed, with efficiencies exceeding 85%. The good reusability shown by the H_3PO_4 -activated adsorbents suggests significant potential for industrial application; namely, in the removal emerging contaminants from urban wastewater. It should be noted that the adsorption efficiency decreased after the fifth cycle, indicating a gradual reduction in performance over time (although it remained above 85% in the performed experiments). This study aims to achieve the goal of zero waste and contribute to the circular economy through the sustainable use of residual biomass.

Keywords: adsorption; biomass-derived activated bioadsorbents; methylene blue; methyl orange; olive stones; pine nut shells

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1. Introduction

1.1. Water Pollution

Water is the most crucial resource in the global economy, essential for nearly all aspects of our lives. Despite covering 70% of the Earth's surface, only about 0.7% of water is suitable for human uses [1].

Agricultural and industrial activities have the potential to pollute water with a variety of compounds, including emerging contaminants, that can be harmful to the environment, as well as human and animal health. As a result, these compounds must be monitored for safety, even at very low concentrations.

The sources of emerging contaminants in water are diverse. Human activity is considered the main cause of pollution, with urban wastewater being a significant source of contaminant emissions.

The risk of water pollution is assessed by considering the hazard, toxicity, and concentration of the pollutants present in water. Water pollutants include pharmaceuticals for human and veterinary use, dyes, pesticides, antiparasitics, and various biocides; additives in materials used as antioxidants, flame retardants, plasticizers, protectors, and anti-corrosives; and household products such as detergents, cosmetics, fragrances, creams, and drugs. The textile industry, which employs cationic and anionic dyes alongside other chemicals, consumes an average of 200 L of water per kg of fabric [2], and thus ranks as the fourth largest consumer of water at the sector level [3]. The textile sector is also the third largest source of wastewater, accounting for around 20% of global industrial wastewater pollution [4]. Even though various highly efficient treatments that remove the majority of pollutants are utilized, the treated water still contains organic compounds that are discharged into water bodies, posing a threat to aquatic ecosystems and human health [5]. Furthermore, pharmaceuticals and their derivatives cause diffuse pollution in various water sources [6], even at very low concentrations [7]. Consequently, drinking water coming from polluted rivers and aquifers can potentially lead to health problems and possibly even severe and/or chronic diseases [8]. These pollutants—known as emerging pollutants or micro-pollutants—are not currently regulated at the state level to limit their presence in water, however, such regulations are expected to be implemented soon. In fact, the European Union Directive 2024/3019 [9], which states that emerging contaminants should not be present in wastewater, is in the process of being transposed into national law. Furthermore, the European Commission establishes a watch list of substances of concern in water intended for human consumption every two years [10]. Due to their low concentrations, emerging pollutants are difficult to detect and conventional technologies used in municipal wastewater plants (WWTPs) have limited ability to remove these pollutants [11].

Water quality is assessed through a series of parameters that help to identify organic contaminants that may be present in the water; for example, color, turbidity, odor, and taste are crucial parameters for evaluating water quality. Color is an organoleptic parameter outlined in Royal Decree 140/2003 [12], which sets health standards for the quality of drinking water and mandates the analysis and control of water to ensure its safety for consumption. The color of water can be influenced by organic materials, natural substances from the soil, or chromophoric metal ions that are dissolved/suspended in the water. Turbidity refers to solids suspended in the water, while true color pertains only to dissolved substances. Additionally, factors such as pH and temperature can also influence the color of water.

1.2. Adsorbents and Adsorption

The growing concern over wastewater pollution has led to the development of technologies and processes to effectively remove organic pollutants from wastewater. It is crucial that these technologies do not have a negative environmental impact; they should be ecofriendly, sustainable, and economically feasible.

Research has shown that the UV/H₂O₂ degradation method can completely break down and mineralize azo dyes [13], and methyl orange has been successfully degraded using this method with gamma irradiation [14]. Studies utilizing electrocoagulation have also been conducted to reduce the color and turbidity of textile wastewater [15]. Photocatalysis is known for its high efficiency, low energy consumption, prevention of secondary pollution, and simplicity of operation [16]. It enables the complete degradation of cationic and anionic dyes such as methyl orange and methylene blue using silica–titania fibers [17]. Microwave catalysis is also gaining recognition as an effective technique for water treatment. It offers fast and uniform heating without temperature gradients, low energy consumption, short reaction times, and high efficiency in degradation of methyl orange [18,19] and methylene blue [19].

Adsorption is considered one of the best methods for removing emerging pollutants from wastewater, thus improving water quality and removing color, due to its flexibility, affordability, and ease of use [20]. Adsorbents, in general, are effective and can be regenerated [21,22]. Nevertheless, adsorption simply transfers the pollutant to a solid phase without causing degradation [23]. Waste organic and inorganic materials, as well as synthetic materials, have been used as adsorbents, for example, natural organic adsorbents including sugarcane bagasse [24], coconut fiber [25], and sawdust [26] and inorganic adsorbents such as sand [27], ash [28], and clays [29] are commonly used. Additionally, commercial synthetic or artificial adsorbents such as the polymeric materials polyurethane [30], polyethylene [31], and nylon fibers [32] are also available.

In the literature, several authors have studied the removal of emerging pollutants from wastewater through adsorption using conventional adsorbents [33–36]. However, these conventional adsorbents are expensive, have low biodegradability, and require additional treatment.

As the adsorption properties of activated carbons rely on the functional groups generated through activation processes, several approaches have been proposed for the preparation of biomass-derived activated carbons. Simple washing and drying of olive stones yield low surface area [37], while carbonization of pine nut shells under anoxic conditions results in a slightly larger surface area [38]. Chemical activation of lignocellulosic wastes—typically using acids such as phosphoric acid, alkalis such as potassium or sodium hydroxide, or metallic salts such as zinc chloride—can enhance the porous structure of the carbon [39]. Activation with phosphoric acid results in the production of highly porous activated carbon containing micropores and mesopores [40]. While activation of olive stones via ZnCl₂, H₃PO₄, and KOH provides similar surface areas [41]. The use of phosphoric acid results in less environmental and toxicological pollution than zinc chloride and the associated process also requires a lower activation temperature than that for potassium hydroxide [39]. Regarding chemical activation with alkalis, no significant differences were found in the surface area of activated carbons acquired using sodium hydroxide compared with potassium hydroxide, although it should be noted that potassium hydroxide is more expensive and more environmentally hazardous [39]. The combination of chemical activation followed by carbonization under a nitrogen atmosphere enhances the surface area and adsorption capacity [41]. Hydrothermal carbonization produces hydrochar from wet waste biomass using subcritical water at moderate temperatures (e.g., below 250 °C, pressures lower than 50 bar, and residence time varying from minutes to days [42–44]. The fundamental advantages include the possi-

bility of processing wet biomass without previous drying [45] and the use of moderate temperatures [46]. Nevertheless, there are also drawbacks, such as a low resulting surface area and a lengthy reaction time [47]. An alternative method to increase the surface area is solvothermal carbonization, which involves organic and inorganic solvents, ionic liquids, and deep eutectic solvents [48]. The main disadvantages of this approach are the significant energy consumption due to the required high temperatures, as well as the use of expensive and pollutant solvents, which are difficult to remove [49]. Another method to enhance the surface area is through combining hydrothermal carbonization with subsequent chemical activation [50].

This work focuses on the use of non-conventional adsorbents due to their low cost, renewability, local availability in large quantities, and high adsorption capacity. Various studies on non-conventional adsorbents can be found in the literature, including those derived from agricultural biomass wastes [21,22], industrial wastes [51–53], and nanostructured materials [54]. Additionally, some relevant studies in the literature have explored the use of algae and clays, both of which have demonstrated promising results [55].

In this study, two non-conventional adsorbents—biomass pine nut shells and olive stones—were selected due to the particular interest in their ability to remove pollutants and improve water quality following their activation. These two selected adsorbents are waste materials from the food industry and human activities, which are produced in large quantities annually and are available at low cost. The utilization of these waste materials in practical applications would contribute to compliance with the Spanish 7/2022 Waste Law [56], aiming to achieve the objective of a zero-waste economy. Various aspects of the adsorbents—including their equilibrium properties—and the results of adsorption studies (including kinetic and thermodynamic studies) are examined, considering different initial adsorbate and adsorbent concentrations. These two adsorbents were activated using two different procedures: chemical activation via sodium hydroxide or phosphoric acid, followed by thermal treatment. They were then utilized for the adsorption of two organic pollutants to assess their adsorption capacity and efficiency. Activation with phosphoric acid leads to the formation of particulate and volatile byproducts, increasing the number of pores in sites previously occupied by the material and expanding micropores and mesopores in activated carbon. It has been previously shown that activated carbon produced from lignocellulosic biomass waste via phosphoric acid activation was highly porous [39]; in contrast, chemical activation with sodium hydroxide created a high number of micropores on the surface of the activated carbon [39].

1.2.1. Adsorbent 1: Waste Biomass—Pine Nut Shells

The stone pine (*Pinus pinea* L.) is a typical Mediterranean species, with the main agricultural activity relating to stone pine being the production of pine nuts. It is cultivated over 650,000 hectares on the Iberian Peninsula, representing two-thirds of its global cultivation area and providing around 70% of the pine nuts produced worldwide. Pine nut shells, accounting for over 80% of the weight of pine nuts, are a major byproduct of the pine seed industry.

1.2.2. Adsorbent 2: Waste Biomass—Olive Stones

After the production of olive oil in oil mills, 80% waste (olive pomace and olive mill wastewater) is generated on the basis of the original olives. The olive stone, representing between 18% and 22% of the total weight of the olive fruit [57], is a significant byproduct of olive oil and table olive production, accounting for a global annual generation exceeding 4 million tons [58].

These biomasses are also used for bioenergy applications [59,60] and pharmaceutical uses [61,62].

1.3. Adsorbates

To evaluate the adsorption capacity of activated adsorbents derived from waste pine nut shells and olive stones, a study was conducted to assess their effectiveness in removing two pollutants: methylene blue and methyl orange. These pollutants are commonly found in wastewater at very low concentrations and are considered emerging pollutants.

1.3.1. Adsorbate 1: Methylene Blue

Methylene blue (also known as basic blue 9) refers to tetramethylthionine chloride, or 3,7-bis(dimethylamino)phenazonium chloride, a cationic organic dye with the chemical formula $C_{16}H_{18}ClN_3S \cdot xH_2O$ (usually $x = 3$) (Figure 1a). It is a granular solid with a dark green color and copper luster that turns blue when dissolved in water. Methylene blue is a redox indicator, changing from a blue color under oxidizing conditions to colorless under reducing conditions. Methylene blue has various important medical applications such as for the treatment of methemoglobinemia; as a topical antiseptic, internal healing agent, and surgical dye; and as a dye for microscopic observation, in addition to its potential use in neurodegenerative diseases under study, and as a dye in [63]. In addition, it is widely used to assess water quality, because it is an indicator of organic water pollution and for evaluating the adsorption capacity of adsorbents for wastewater treatment, suitable for specific applications of molecules of a similar size. Methylene blue is also a reference sorbate for determining the external cation exchange capacity in soils and other natural materials [64]. Additionally, it is considered a toxic pigment, harmful to both human and animal health [65].

1.3.2. Adsorbate 2: Methyl Orange

Methyl orange is the sodium sulfonic acid salt of 4-dimethylaminoazobenzene, with the chemical formula $C_{14}H_{14}N_3NaO_3S$ (Figure 1b). It is an anionic azo dye which is frequently used as a pH indicator, changing color from red to orange-yellow between pH 3.1 and 4.4. Methyl orange is also utilized in pharmaceutical preparations, as a dye for fabrics, and for staining microscope samples [66]. Methyl orange has mutagenic toxicity, which can lead to cancer and genetic damage [20,67]. Both of the above mentioned dyes are present in wastewaters [68]. Consequently, these harmful substances should be effectively removed before discharging. Nevertheless, these compounds are difficult to remove from wastewater due to their aromatic structure, high organic content, non-biodegradability, and light resistance [5].

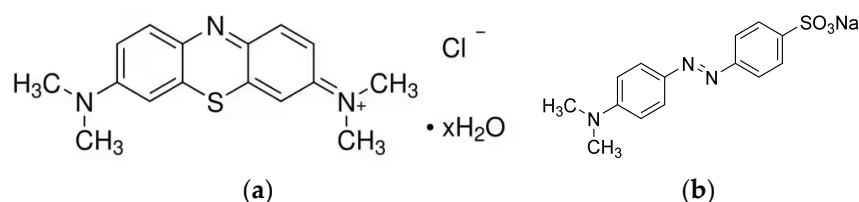


Figure 1. Molecular structure of (a) 3,7-bis(dimethylamino)phenazonium chloride, (b) 4-dimethylaminoazobenzene.

There are studies in the literature on the use of these two adsorbents in water with pine nut shells [69] and olive stones [70]. In particular, several authors have published research on the adsorption of methylene blue onto pine nut shells and olive stones. Naushad et al. [71] and Sverguzova et al. [72] reported the adsorption performance of methylene blue on pine nut shells treated with sodium hydroxide, while Kim et al. [38] studied the performance of pine nut shells that were thermally activated in a tubular

furnace with N₂ up to 700 °C. The adsorption of methylene blue onto adsorbents derived from olive stones has been reported for raw material [37]; after thermal activation in the absence of air using a vertical reactor at temperatures up to 900 °C [73]; activated with H₃PO₄ [74]; and chemically activated with ZnCl₂, H₃PO₄, and KOH followed by a thermal treatment at 600 °C in a vertical tubular reactor under a nitrogen atmosphere [41]. However, there remains a gap in the literature regarding the adsorption of methyl orange onto pine nut shell- and olive stone-based adsorbents, despite existing studies using other adsorbents [20,75–77].

According to the thermodynamic analyses conducted by Alardhi et al. [37], Ozcan et al. [41] and Kim et al. [38] the adsorption of methylene blue onto adsorbents obtained from olive stones is spontaneous and endothermic; however, another study described the process as exothermic [78]. The adsorption of methyl orange has been spontaneous and exothermic [7], although other authors reported its endothermic adsorption onto commercial activated carbon fiber [79]. Even though the adsorption process of both dyes is irreversible, due to the positive entropy values, the very low Gibbs free energy value indicates a percentage of desorption. Therefore, the dye adsorption process is neither controlled by entropy nor enthalpy [44].

2. Materials and Methods

2.1. Activation of the Adsorbents and Characterization of Waste Biomass

Two low-cost biomass-based adsorbents were prepared from lignocellulosic biomass waste—specifically pine nut shells and olive stones—through thermochemical activation. Initially, the biomass waste was ground to reduce the particle size using a Fritsch Pulverisette 15 mill (Fritsch, Idar-Oberstein, Germany). Three fractions with particle diameters of $d_p = 0.09\text{--}0.63$, $0.63\text{--}1$, and $1\text{--}2$ mm were separated using a Filtra FTI-0300 (Filtra Vibracion, S.L., Badalona, Spain) sieving machine.

The waste biomasses were characterized according to their density, ultimate and proximate analysis, higher heating value (HHV), and lower heating value (LHV) using standard methods, and the results are listed in Table 1.

Table 1. Ultimate and proximate analyses of pine nut shells and olive stones.

	Pine Nut Shells	Olive Stones	Standard	Equipment
Density (kg/m ³)	1212	1154		
Ultimate analysis (wt% d.b.)				
C	51.36	50.92	ASTM D4239 [80]	LECO CHN-2000 (LECO Corporation, St. Joseph, MI, USA)
H	5.78	6.53	ASTM D4239 [80]	LECO CHN-2000 (LECO Corporation, St. Joseph, MI, USA)
O	41.34	40.62	By difference	
N	0.25	0.27	ASTM D4239 [80]	LECO CHN-2000(LECO Corporation, St. Joseph, MI, USA)

S	0.02	0.04	ASTM D5865 [81]	LECO S-632 (LECO Corporation, St. Joseph, MI, USA)
Proximate analysis (wt% d.b.)				
Volatile matter (VM)	73.69	76.40	ASTM D7582 [82]	LECO TGA701 (LECO Corporation, St. Joseph, MI, USA)
Fixed carbon (FC)	25.06	21.98	By difference	LECO TGA701 (LECO Corporation, St. Joseph, MI, USA)
Ash	1.25	1.62	ASTM D7582 [82]	LECO TGA701 (LECO Corporation, St. Joseph, MI, USA)
Moisture	7.94	13.12	ASTM D7582 [82]	LECO TGA701 (LECO Corporation, St. Joseph, MI, USA)
Heating values				
HHV (kcal/kg)	4922	4800	ISO 1928 [83]	IKA C4000 (IKA Group, Staufen, Germany)
LHV (kcal/kg)	4639	4500	ISO 1928 [83]	IKA C4000 (IKA Group, Staufen, Germany)

The two adsorbents were activated via two different methods: using an alkali sodium hydroxide solution and a phosphoric acid solution (Sigma-Aldrich, St. Louis, MO, USA). The activation processes using each method are illustrated in Figure 2.

In the sodium hydroxide method each solid fraction was washed with deionized water at 85 °C while stirring for 2 h. The solutions were then filtered in a Buchner funnel with a filter flask connected to a vacuum pump, and then dried in an oven (Selecta VACIOTEM-T, Abrera, Spain) at 105 °C for 24 h. The solids were impregnated with a 1 M NaOH solution, using a mass ratio of the activating agent to the dry biomass of 1:1.75 (35%), and stirred at 500 rpm for 30 minutes. Following filtering and drying of the solutions in an oven for 24 h at 105 °C, the solid fractions were thermally activated and carbonized in a horizontal tubular furnace (Hobersal ST100, Caldes de Montbui, Spain), consisting of a ceramic tube (inner diameter 40 mm, length 1000 mm, and gas outlet port 2.7 mm). The furnace was heated at a heating rate of 7 °C/min; from 200 °C, a N₂ flow rate of 60 mL/min (empty tube velocity 4.8 cm/min, outlet velocity 17.5 cm/s) was fed and once the temperature reached 550 °C, it was maintained for 2 h. The temperature of 550 °C was selected as it resulted in 20% higher adsorption performance, compared with other temperatures tested in the range 400–700 °C. After thermal treatment, the material was neutralized with 0.1 M HCl, washed with deionized water until a pH of 7 was achieved (measured using a calibrated pH meter, accuracy ± 0.1,) filtered using a Buchner funnel connected a filter flask with a vacuum pump, and then dried in an oven at 105 °C for 24 h.

The phosphoric acid method involved first washing each solid fraction with deionized water at 85 °C while stirring for 2 h. After filtering, each solid fraction was impregnated with a 36% H₃PO₄ solution using a 1:2 mass ratio of the activating agent to the dry biomass, stirring at 85 °C for 2 h at 500 rpm. A filter flask connected to a vacuum pump was used to filter the solutions in a Buchner funnel, followed by drying in an oven at

105 °C for 24 h. Each sample underwent thermal activation in a tubular furnace according to the procedure detailed above. The samples were washed with deionized water until pH 7 was reached and filtered through a Buchner funnel connected to a filter flask with a vacuum pump. Finally, all of the materials were dried in an oven at 105 °C for 24 h.

The utilized adsorbents were named as follows: raw pine nut shells (PNS), raw olive stones (OS), pine nut shells activated with NaOH (PNSNC), pine nut shells activated with H_3PO_4 (PNSPC), olive stones activated with NaOH (OSNC), and olive stones activated with H_3PO_4 (OSPC).

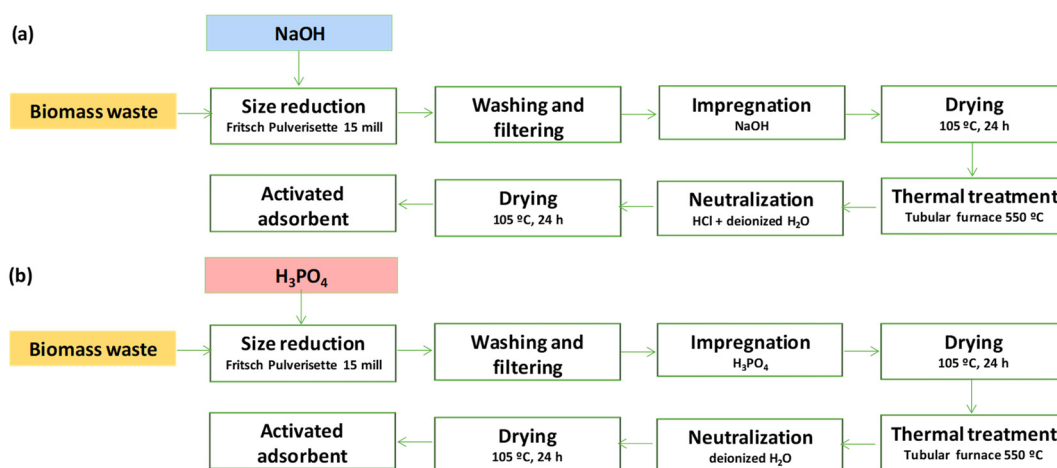


Figure 2. Block diagram of the preparation of adsorbents. (a) using NaOH, (b) using H_3PO_4 .

The specific surface area of the activated adsorbents was determined using the Brunauer–Emmett–Teller (BET) method, analyzing adsorption-desorption N_2 isotherms at 77 K with a BELSORP-max II (MicrotracBEL Corp., Osaka, Japan) adsorption analyzer. Before testing, the samples were degassed under vacuum using a turbomolecular pump (minimum vacuum 10^{-7} mbar and flow of 15L/min) for 12 h at 100 °C with a heating ramp of 10 °C/min.

The point of zero charge (pH_{PZC}) of the adsorbents was determined as it is a significant measure of the surface charge and the affinity of an adsorbent for ionic species. To determine this, the pH of 50 mL solutions of deionized water was adjusted to between 2.0 and 11.0 by adding the required amounts of 0.1 M HCl or 0.1 M NaOH, following which 0.5 g of the adsorbent material was added to each of these solutions. After stirring for 48 h at room temperature, the samples were filtered and the final pH value of the aqueous solutions was measured.

The functional groups on the activated carbons were analyzed via FTIR spectroscopy (Shimadzu IRAffinity-1S with a Golden Gate Diamond ATR unit, Kyoto, Japan). Each spectrum was obtained by taking 32 scans in the 4000–600 cm^{-1} range.

The structural disorder of the activated carbons was determined using Raman spectroscopy (Confocal microscope Raman Renishaw inVia Qontor with a CCD detector, Wotton-under-Edge, UK).

2.2. Adsorption Process

The adsorption process was conducted in accordance with the ASTM D3860-98 standard [84]. Solutions containing 100 mL of methylene blue or methyl orange (Sigma-Aldrich) with initial concentrations ranging from 5 to 50 mg/L were prepared. Subsequently, a mass of adsorbent derived from pine nut shells or olive stones activated via NaOH or H_3PO_4 , referred to as PNSNC, PSNPC, OSNC, and OSPC, respectively, ranging from 1 to 5 g/L was added to the solutions. The mixtures were stirred at 500 rpm at room

temperature and liquid samples were collected at regular time intervals. The samples were then centrifuged (Eppendorf 5804 R) at 3600 rpm for 20 minutes and filtered. Every adsorption process was performed three times under each experimental condition to ensure reliability and accuracy. Subsequently, mean and standard deviation values were calculated.

Next, the concentrations of methylene blue and methyl orange were determined from the absorbance of the samples using UV-Vis spectroscopy, based on the concentration–absorbance calibration lines of methylene blue and methyl orange obtained at various concentrations.

For this purpose, several solutions with known concentrations of methylene blue and methyl orange ranging from 0.5 to 50 mg/L were prepared. The absorbance of methylene blue and methyl orange in these solutions was determined using UV-Vis spectroscopy with a SHIMADZU UV-1280 spectrophotometer. This involved passing a light beam at a single wavelength or multiple wavelengths through the sample and measuring the amount of light absorbed or transmitted. Following zeroing with deionized water, a wavelength scan was conducted in the range of 190–1100 nm to determine the spectra and the wavelength corresponding to the peak of highest absorbance for methylene blue and methyl orange. The maximum absorbance of methylene blue was found at a wavelength of 665 ± 1.0 nm at pH 7.3. As an example, Figure 3 shows the UV-Vis spectra for methyl orange at pH levels of 7.3, 5.5, and 3.5. The maximum absorbance of methyl orange was observed at a wavelength at 464 ± 1.0 nm at pH 7.3, at 466 ± 1.0 nm at pH 5.5, and at 470 ± 1.0 nm at pH 3.5. Therefore, it remained in anionic form at all pH levels studied. The experimental absorbance values obtained for each solution and the concentrations of methylene blue and methyl orange were plotted on concentration–calibration straight lines with high coefficients of determination ($R^2 = 0.9991$ and $R^2 = 0.998$, respectively).

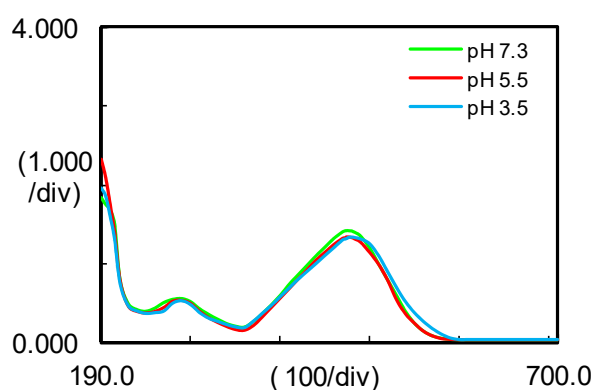


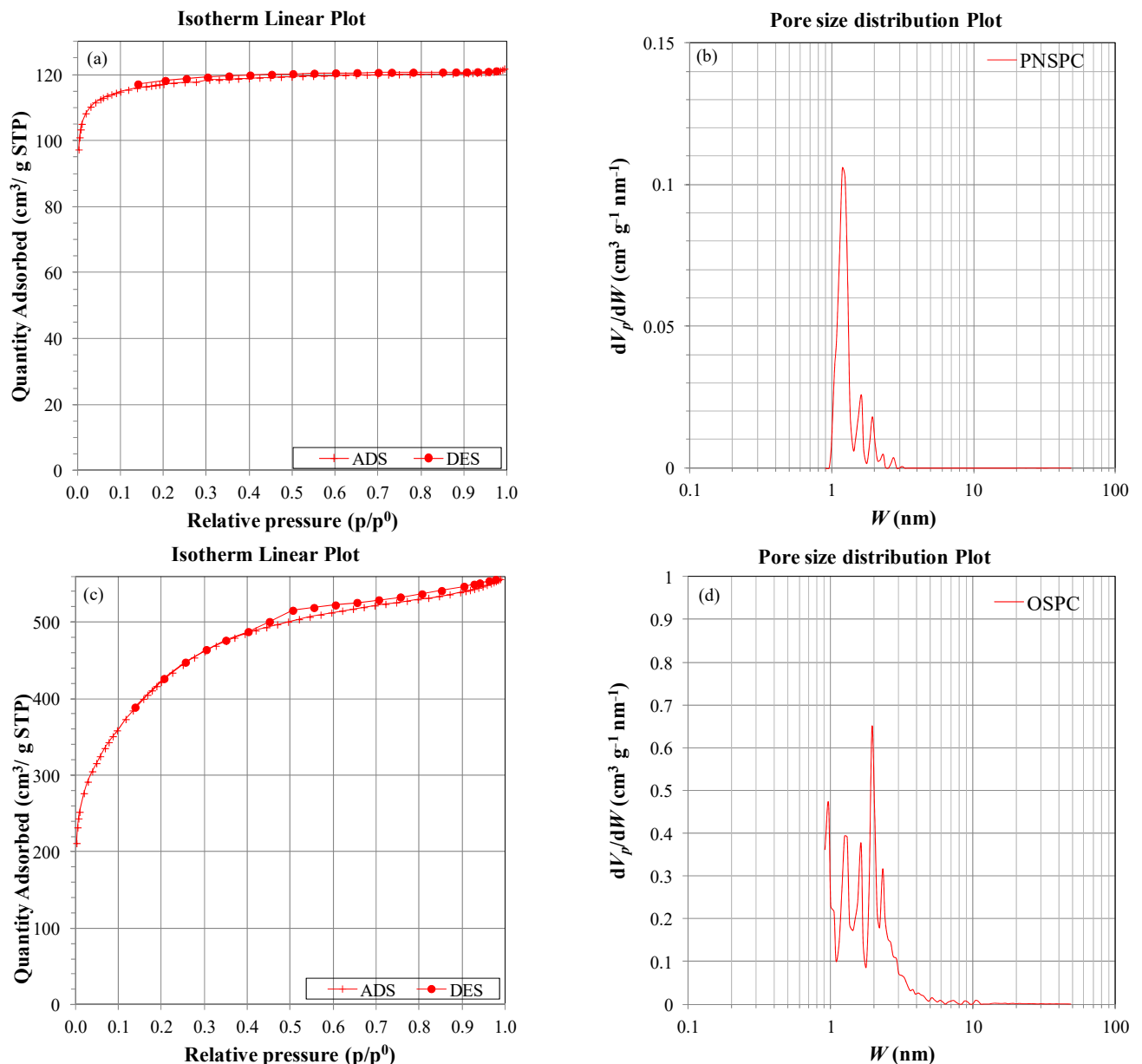
Figure 3. UV-Vis spectra of methyl orange at pH levels of 7.3, 5.5 and 3.5.

3. Results and Discussion

3.1. Characterization of the Activated Adsorbents

Figure 4 presents the adsorption–desorption N_2 isotherms of adsorbents derived from pine nut shells (Figure 4a) and olive stones (Figure 4b) activated with H_3PO_4 , as well as that of commercial activated charcoal (Panreac) (Figure 4c). The BET surface areas of the pine nut shell and olive stone adsorbents activated with H_3PO_4 , as well as the commercial activated charcoal were 464, 1535, and 921 m^2/g , respectively. In contrast, the BET surface areas of pine nut shells and olive stones adsorbents activated with NaOH were 192 and 228 m^2/g , respectively. The pore size distribution determined according to the nonlocal density functional theory (NLDFT) is plotted in Figure 4 for adsorbents derived

from pine nut shells (Figure 4d) and olive stones activated using H_3PO_4 (Figure 4e) and for commercial activated charcoal (Figure 4f). The average pore diameters are 1.6126, 2.2264, and 2.9418 nm and the total pore volumes are 0.186900, 0.854342, and 0.6775 cm^3/g , respectively. Thus, the adsorbent obtained from olive stones activated via H_3PO_4 had a BET surface area more than three times higher than that of similarly activated pine nut shells and 66% higher than that of commercial activated charcoal. It also had a total pore volume almost five times higher than that of the activated pine nut shells adsorbents and almost 30% higher than that of the commercial activated charcoal, indicating a high adsorption capacity. In addition, its slightly larger average pore diameter compared with the pine nut shells adsorbent facilitates rapid diffusion, similarly to the commercial activated charcoal. The surface areas obtained for pine nut shells thermally activated with NaOH was higher than that reported for pine nut shells chemically activated with NaOH by Nashuad et al. [71] (176 m^2/g) and thermally activated by Kim et al. [38] (47.6 m^2/g). Similarly, the surface area found for olive stones activated with H_3PO_4 was greater compared with that reported by Wafaa et al. [74] for those chemically activated with H_3PO_4 (74.86 m^2/g) and by Ozcan et al. [41] for those thermochemically activated with H_3PO_4 (970 m^2/g).



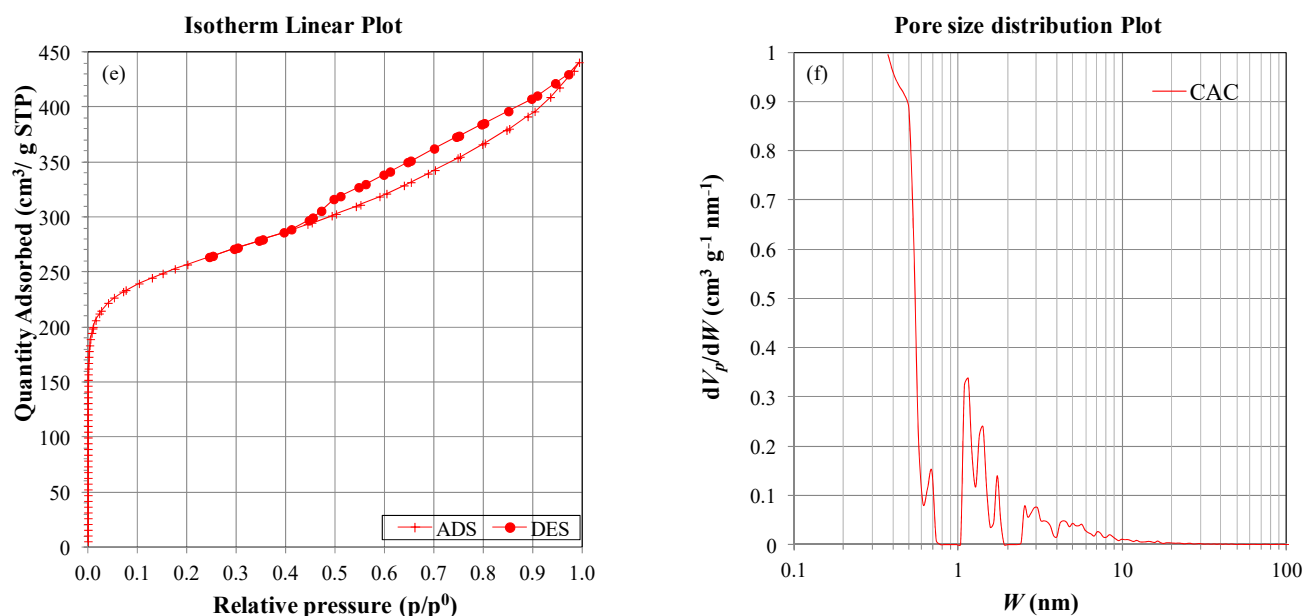


Figure 4. Adsorption–desorption isotherm of N₂ of adsorbent activated with H₃PO₄ derived from (a) pine nut shells, (b) olive stones, and (c) commercial activated charcoal. Pore size distribution (d) pine nut shells, (e) olive stones, and (f) commercial activated charcoal.

The interactions between both of the dyes and the adsorbent surfaces is primarily driven by electrostatic attraction. Methyl orange (MO), as an anionic dye, carries negatively charged sulfonate groups, and, thus, its adsorption is most efficient when the adsorbent surface is positively charged (often under acidic conditions). As a cationic dye, methylene blue (MB) dissociates in water into positively charged MB⁺ species. The strength of this interaction depends on the pH relative to the adsorbent's pH_{pzc}. At low pH (<pH_{pzc}) the surface becomes protonated and positively charged, enhancing the attraction of methyl orange anions; meanwhile, at high pH (>pH_{pzc}) the surface becomes negatively charged, leading to electrostatic repulsion and a significant decrease in adsorption efficiency. In addition to electrostatic forces, the aromatic rings in both dyes can interact with aromatic structures on the activated carbon through π – π electron dispersions. Likewise, in the case of MB, hydrogen bonding can occur between the nitrogen atoms in the dye molecule and hydroxyl or carboxyl groups on the carbon surface. The points of zero charge (pH_{pzc}) of the PNSNC, PNSPC, OSNC, and OSPC adsorbents were 6.8, 6.5, 6.9, and 6.7, respectively. To optimize adsorption, the initial pH was set at 7.3 for methylene blue as, at a pH higher than the zero charge point, the adsorbent is negatively charged and has a greater affinity for adsorbing cationic species such as methylene blue. As the adsorbent is positively charged at pH values below the zero charge point and has a higher affinity for adsorbing negatively charged species such as methyl orange, the initial pH values for methyl orange were set at 3.5 and 5.5 [41].

The FTIR spectra of activated carbons derived from pine nut shells (PNSPC, PNSNC) and olive stones (OSPC, OSNC) were analyzed to identify characteristic functional groups (Figure 5); the commercial activated charcoal was also included as a reference. All spectra displayed absorption bands characteristic of activated carbons containing aromatic structures and oxygen-containing surface functional groups, indicating successful activation and surface modification of the carbon framework [85–87]. All samples exhibited a broad absorption band in the 3200–3600 cm⁻¹ region, which corresponds to the OH-stretching vibrations of hydroxyl groups in phenols, carboxylic acids, or adsorbed water. The intensity of this band varied considerably between the samples, being strongest for PNSNC, suggesting significant differences in surface hydroxyl con-

tent and overall polarity. Weak bands appearing around 2850–2980 cm^{-1} are generally associated with aliphatic C–H stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ groups, indicating the presence of residual aliphatic structures or surface-bound hydrocarbons [86]. The spectral region between 1750 and 1680 cm^{-1} is associated with C=O stretching vibrations of oxygenated functional groups such as carboxylic acids. These bands were weak in PNSNC, moderately intense in PNSPC and OSNC, and clearly pronounced in OSPC, reflecting an increasing degree of surface oxidation. A band centered around 1580–1620 cm^{-1} was observed in all samples and was assigned to aromatic C=C stretching vibrations, confirming the predominance of conjugated aromatic structures typical of activated carbons. Absorptions in the 1380–1450 cm^{-1} range are attributed to C–H bending and O–H deformation vibrations, while bands in the 1250–1000 cm^{-1} region are assigned to C–O stretching vibrations of phenols, ethers, alcohols, and ester groups [86,87]. The reference sample exhibited the highest overall absorbance intensity and distinct features in the 1900–2100 cm^{-1} region, which are commonly attributed to combination and overtone bands associated with strongly conjugated carbonyl systems or surface complexes in highly functionalized carbons [87]. In contrast, PNSNC sample showed the lowest absorbance and weakest oxygen-related bands, suggesting a higher degree of carbonization and a more graphitic, less polar surface. Overall, the FTIR analysis demonstrated that while all samples shared a common aromatic carbon backbone, their surface chemistry differed markedly. The relative abundance of oxygen-containing functional groups follows the order $\text{PNSNC} < \text{PNSPC} \approx \text{OSNC} < \text{OSPC}$.

On the other hand, differences in the spectra were observed based on the raw material precursor and the chemical activating agent. The H_3PO_4 -activated carbons (PNSPC and OSPC) showed distinct differences when compared with the NaOH-activated samples (PNSNC and OSNC). The former generally exhibited stronger and broader peaks in the region of 1000–1450 cm^{-1} , indicative of a higher concentration of oxygen-containing functional groups (C–O, P–O–C linkages). Conversely, the NaOH-activated carbons (PNSNC, OSNC) displayed more intense bands in the aliphatic C–H region (around 2850–2980 cm^{-1}), suggesting differences in the char structure and the removal of organic matter during the activation process. The raw material also influenced the final surface chemistry. The olive stone-derived samples (OSPC and OSNC) had a notably higher initial signal intensity across the spectrum compared with the pine nut shell samples (PNSPC and PNSNC). This may be due to inherent differences in the initial lignocellulosic composition (e.g., lignin, cellulose, hemicellulose content) of the precursors or different inorganic matter (e.g., ash) content which affects the final carbon structure and functional groups after activation. Specifically, olive stones often produce carbons with significant oxygen content, which aligns with the higher O–H and C=O intensities observed in OSPC and OSNC.

Methylene blue is a cationic dye that exhibits a strong electrostatic attraction to negatively charged adsorbent surfaces, as it possesses positive charges, while methyl orange has an anionic character behavior due to its sulfonate groups, and thus preferentially interacts with protonated or positively charged adsorbents. Therefore, the ionic nature of each adsorbate plays a key role in the performance of the activated carbons.

Carboxyl and phosphate groups can play critical roles in defining the surface chemistry of the adsorbents, as well as their stability and performance. Carboxyl groups significantly increase the surface acidity and electronegativity of activated carbons; this tends to reduce surface polarization, making the adsorbent more effective for attracting solutes through electrostatic interactions, and contributing to improved adsorption capacity. On the other hand, activation with H_3PO_4 leads to the formation of C–O–P bridges that crosslink the structural components of lignocellulosic biomass, preventing shrink-

age of the carbon structure and promoting the development of a mesoporous network, thus enhancing the chemical stability of the activated carbon.

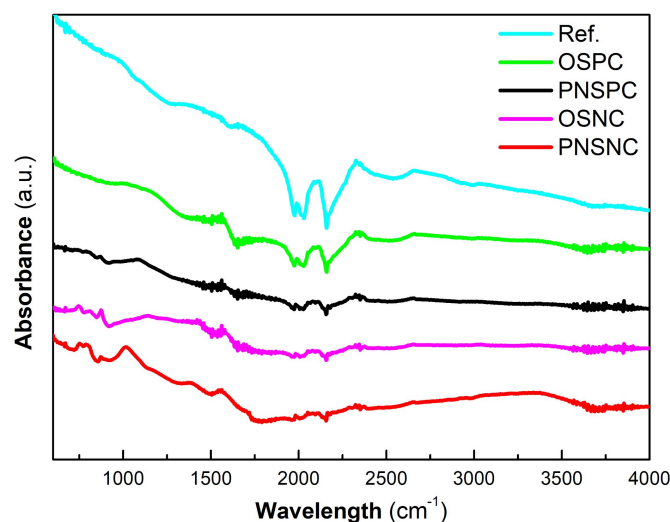


Figure 5. FTIR spectra of the activated adsorbents.

The Raman spectra of the activated carbons (Figure 6) exhibited two prominent bands: the D-band (disorder-induced band around 1350 cm^{-1}) and the G-band (graphitic band around 1580 cm^{-1}), which are characteristic of sp^2 hybridized carbon materials. The intensity ratio of these bands (I_D/I_G) provides a semi-quantitative measure of structural disorder and crystallite size, with a higher ratio indicating greater defect density. Visual analysis of the spectra suggested significant differences in defect density between the samples. All activated carbons (ACs) showed prominent D- and G-bands, and the calculated I_D/I_G ratio values are given in Table 2. The commercial charcoal (Ref.) exhibited the highest I_D/I_G ratio, suggesting a higher density of defects compared with the prepared ACs. Among these samples, OSPC had the highest I_D/I_G ratio, indicative of the most disordered structure. Comparing samples from the same pretreatment (i.e., PNSPC vs. OSPC, and PNSNC vs. OSNC), the raw material appears to influence the final carbon structure. Pine nut shell-derived samples (PNSPC and PNSNC) yielded significantly lower I_D/I_G ratios than the olive stone-derived samples (OSPC and OSNC). Furthermore, the activating agent had a profound impact on the final material structure and surface chemistry. Samples pretreated with H_3PO_4 (PNSPC and OSPC) showed higher I_D/I_G ratios than their NaOH-pretreated counterparts (PNSNC and OSNC), indicating that the H_3PO_4 activation process resulted in a higher concentration of structural defects and more amorphous carbon regions. H_3PO_4 primarily acts as a template for micropore creation and facilitates the formation of C-O-P functional groups, which introduce defects into the carbon lattice. NaOH activation often results in different nitrogen/carbon structures, tending to produce a more ordered graphitic structure.

The existence of multi-mechanistic adsorption process was supported by the FTIR (Figure 5) and Raman (Figure 6) spectral analysis results. As aromatic dyes, π - π interactions played an important role. These interactions enhance the π - π stacking between dye aromatic rings and carbon basal planes in the adsorbents. The Raman spectra confirmed abundant sp^2 -hybridized aromatic domains in the activated carbons, where defective aromatic structures (higher D band) were increased in H_3PO_4 -activated carbons. In particular, the PNSPC and OSPC samples showed the best balance between aromaticity and defect density. Furthermore, electrostatic interactions appear to be dominant in adsorption, especially for MB as a cationic dye. On the other hand, the higher adsorption capacities of the H_3PO_4 -activated carbons (OSPC and PNSPC) could also be due to the

fewer acidic groups created in NaOH-treated samples, which led to weaker electrostatic attraction. Likewise, the presence of hydroxyl, carboxyl, and phosphate groups confirmed via FTIR is related to the hydrogen bonding abilities of the samples, which would be especially relevant for MO due to its anionic nature.

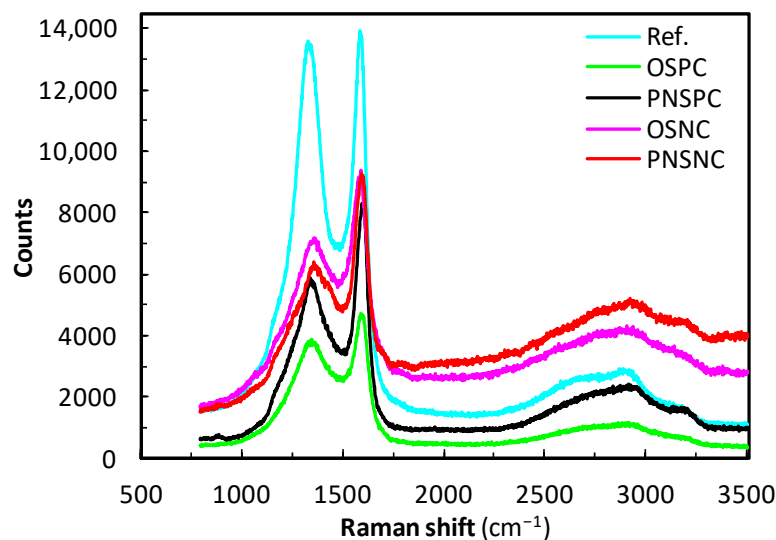


Figure 6. RAMAN spectra of the activated adsorbents.

Table 2. Raman spectroscopic data of activated carbons in the range of 950–1900 cm^{−1}.

Adsorbent	D-Band (cm ^{−1})	G-Band (cm ^{−1})	I _D /I _G Ratio
PNSPC	1342	1603	0.684
PNSNC	1359	1595	0.617
OSPC	1349	1592	0.801
OSNC	1359	1592	0.702
Ref.	1336	1587	0.967

3.2. Adsorption Capacity and Efficiency of the Activated Adsorbents

To determine the adsorption process under different operating conditions, the adsorption capacity and efficiency were calculated using Equations (1) and (2):

$$q = V(C_0 - C)/S \quad (1)$$

$$\eta = (C_0 - C)/C_0 \times 100 \quad (2)$$

where q represents the adsorption capacity (mg g^{−1}), C_0 is the initial concentration of the adsorbate (mg L^{−1}), C is the concentration of the adsorbate at time t (mg L^{−1}), V is the volume of the solution (mL), S is the mass of the adsorbent (g), and η is the adsorption efficiency.

3.2.1. Effect of the Activation Method

The time evolution of the mean experimental values of adsorption capacity and efficiency of pine nut shells without activation (PNS), those activated with NaOH (PNSN), and those activated with H₃PO₄ (PNSPC) during the adsorption of methylene blue and methyl orange with an initial concentration of 10 mg/L on 1 g/L of adsorbent are compared in Figure 7. The error bars indicate the standard deviation from the mean of each of the adsorption experiments (which were performed in triplicate). The adsorption capacity increased over time, initially with a pronounced trend as the adsorbent sites be-

came available, and subsequently presenting an asymptotic trend once the adsorption sites had been saturated for both dyes. As can be observed from Figure 7a,c, the adsorption capacity of pine nut shells, without activation was low, while those of PNSNC and PNSPC were approximately 7 and 19 times higher for MB and 3 and 23 times higher for MO. Additionally, the adsorption efficiency (shown in Figure 7b,d) was very low for raw pine nut shells without activation, being almost 7 and 23 times higher for PNSNC and PNSPC, respectively for MB, and 4 and 25 times higher for MO.

Figure 8 compares the effect of the activation method on the adsorption capacity and efficiency of adsorbents derived from olive stones of methylene blue and methyl orange. Untreated olive stones were found to have low capacity and efficiency, while these values increase by approximately 4 and over 10 times for OSNC and OSPC, respectively.

The adsorption capacity and efficiency of adsorbents made from pine nuts and olive stones were approximately 3 and 2.6 times higher, respectively, when treated with H_3PO_4 compared with $NaOH$. Additionally, while the equilibrium values of adsorption capacity and efficiency for the two adsorbents derived from pine nut shells and olive stone activated with H_3PO_4 were similar, those of olive stones were slightly higher than those of pine nut shells.

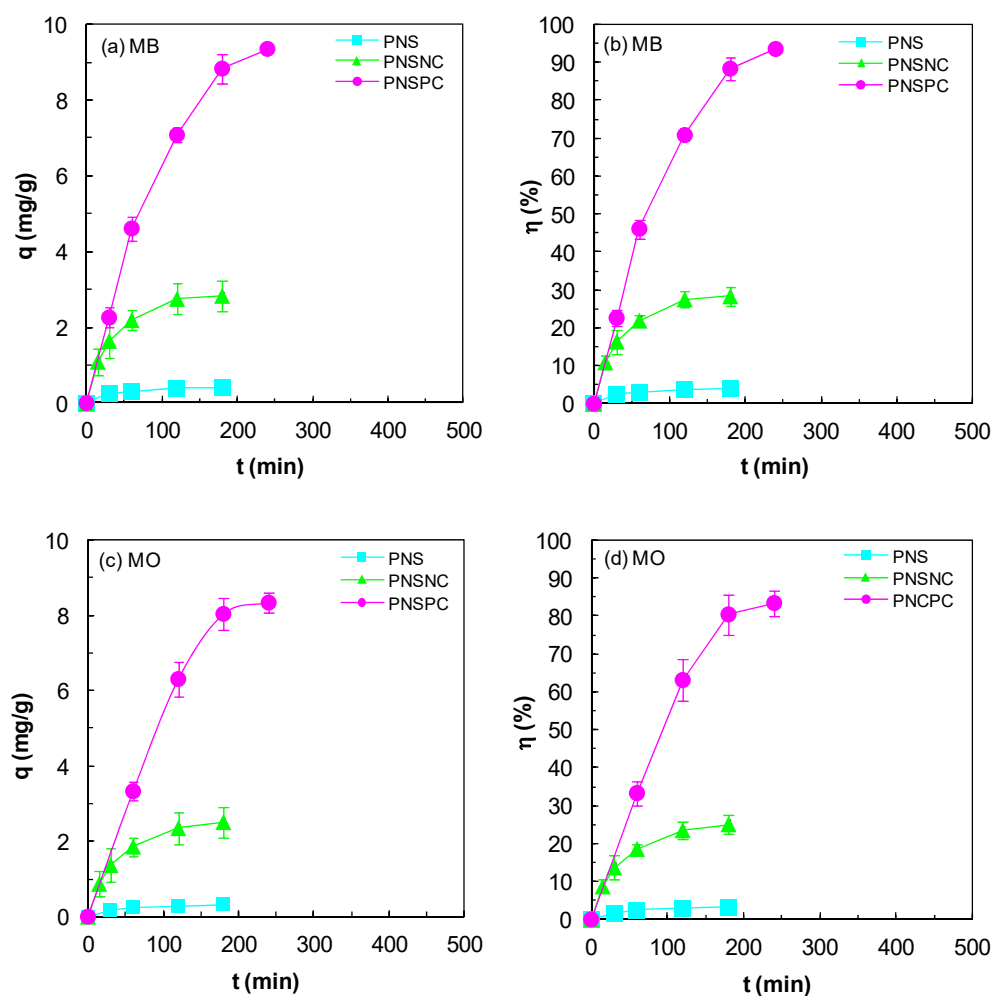


Figure 7. Time evolution of adsorption performance of methylene blue and methyl orange with PNS, PNSNC, and PNSPC by triplicate tests. $C_0 = 10$ mg/L and $S = 1$ g/L (a) adsorption capacity of MB, (b) adsorption efficiency of MB, (c) adsorption capacity of MO, (d) adsorption efficiency of MO.

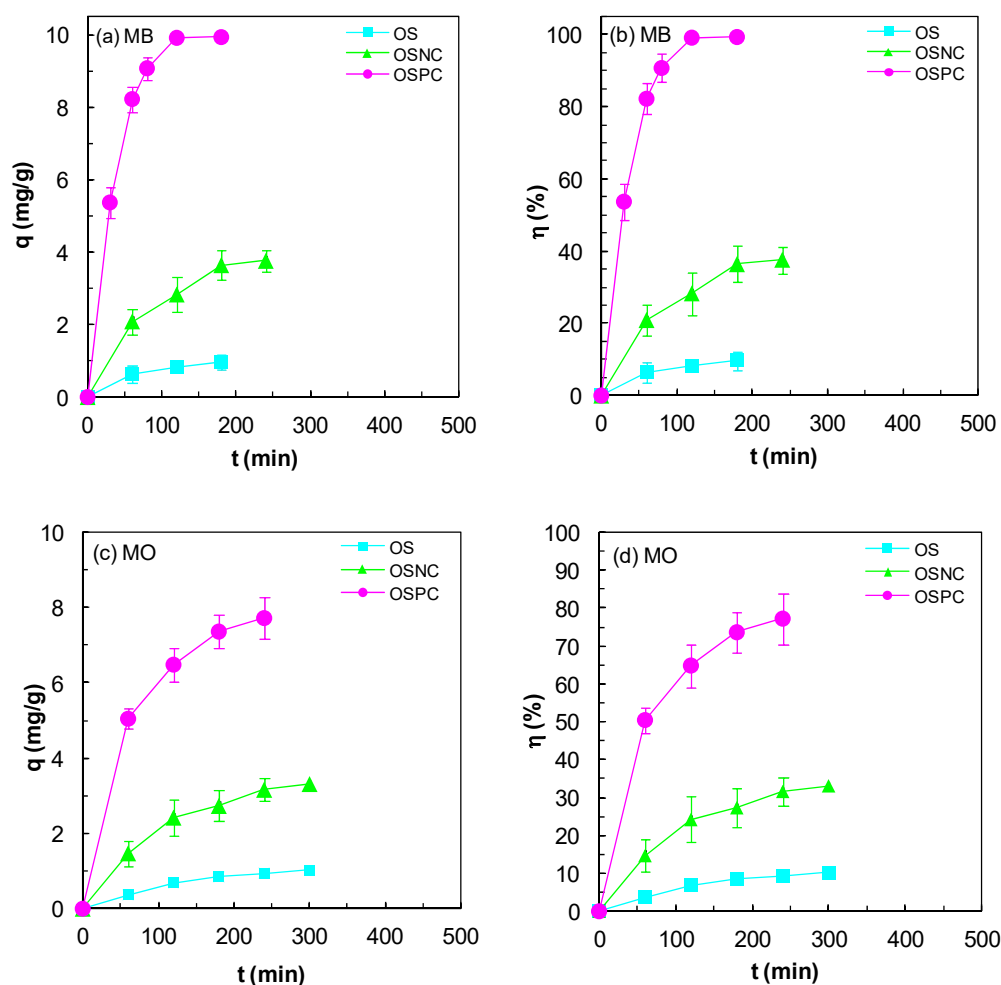


Figure 8. Time evolution of adsorption performance of methylene blue and methyl orange with OS, OSNC, and OSPC by triplicate tests. $C_0 = 10$ mg/L and $S = 1$ g/L (a) adsorption capacity of MB, (b) adsorption efficiency of MB, (c) adsorption capacity of MO, (d) adsorption efficiency of MO.

3.2.2. Effect of the Dye Type

Figure 9 compares the effect of the dye used on the adsorption capacity and efficiency of the PNSPC and OSPC adsorbents (at 1 g/L) for solutions with an initial concentration of 20 mg/L of methylene blue or methyl orange ($\text{pH } 7.3 \pm 0.1$). Although the adsorption capacity and efficiency of the adsorbents for methylene blue were only slightly higher than those for methyl orange (as they have similar molecular weight and particle size) equilibrium was reached faster with methylene blue, especially for OSPC. The difference in adsorption between methylene blue and methyl orange could be explained by the slightly basic pH of the solution during the adsorption process. This is consistent with the literature, which reported that hydrophilic adsorbents exhibit greater adsorption of methylene blue, due to intervening electrostatic forces [88]. As methyl orange is an anionic dye, such conditions would not favor its adsorption at the same intensity [20]. Adsorption was conducted with the methyl orange dye, by adjusting the pH to 5.5 via adding 0.1 M HCl to the solution. It was observed that the adsorption efficiency on 1 g/L of the PNSPC adsorbent was 91.15% while that on the OSPC adsorbent was 97.89%—practically the same values as at pH 7.3. When further adding 0.1 M HCl to the solution to decrease the pH to 3.5, the adsorption efficiency of methyl orange for the PNSPC adsorbent was 93.45% and that for the OSPC adsorbent was 99.13%. Therefore, at pH 3.5, practically the same values were obtained for methyl orange as for methylene

blue at pH 7.3. When the target solution pH was greater than the pH_{pzc} of the four activated carbons (6.5–6.9), the carbon surfaces were predominantly negatively charged. On the other hand, MB (pK_a 3.8) is almost entirely in its cationic form at pH 7.3, while MO (pK_a 3.47) exists in its anionic form. Therefore, the observed difference in adsorption capacity is primarily driven by the nature of the electrostatic forces (attractive in the case of MB and repulsive for MO) between the dye molecules and the adsorbent surface. In fact, there is a strong electrostatic attraction between the positively charged MB cations and the negatively charged activated carbon surface, which makes the adsorption process spontaneous and highly efficient at neutral or basic pH. Conversely, there is electrostatic repulsion between the negatively charged MO anions and the negatively charged carbon surface, such that its adsorption is more unfavorable at a pH of 7.3, and the experimental pH between 6.5 and 5.5 was found to be more favorable for the MO.

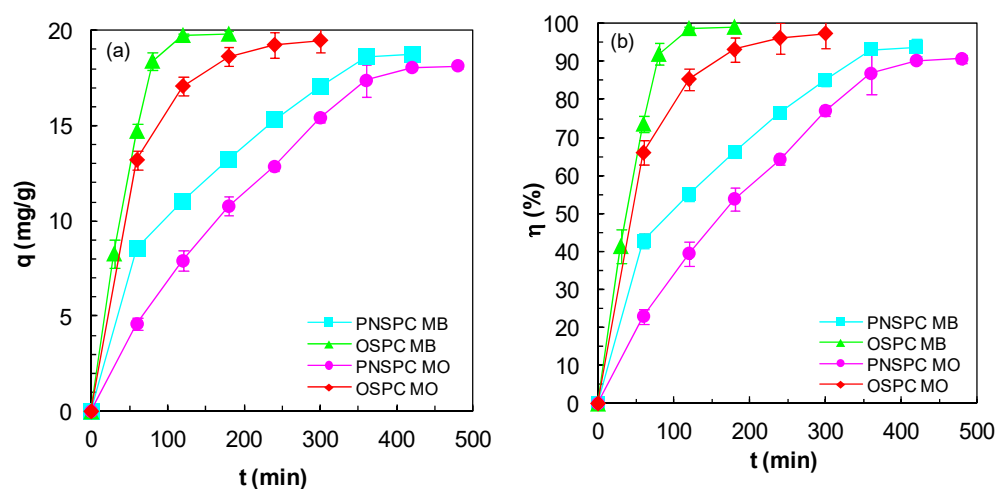


Figure 9. Time evolution of adsorption performance of methylene blue and methyl orange with PNSPC and OSPC adsorbents by triplicate tests. $C_0 = 20$ mg/L, $S = 1$ g/L. (a) Adsorption capacity, (b) adsorption efficiency.

Figure 10 shows samples of the methylene blue and methyl orange solutions (with an initial concentration of 20 mg/L) before and during adsorption at pH 7.2 onto OSPC adsorbent, in which the color degradation is very noticeable.

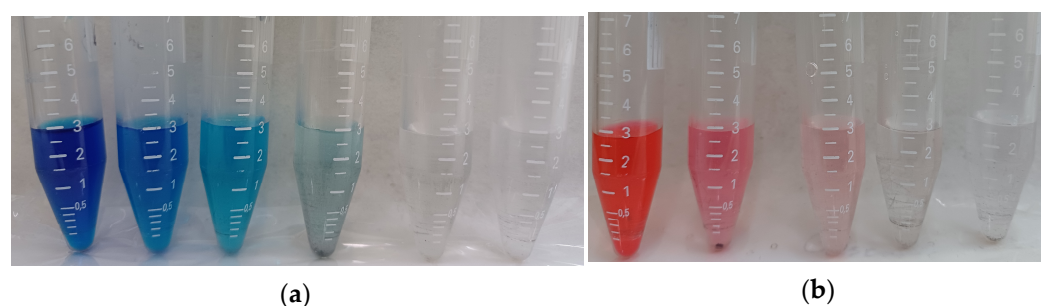
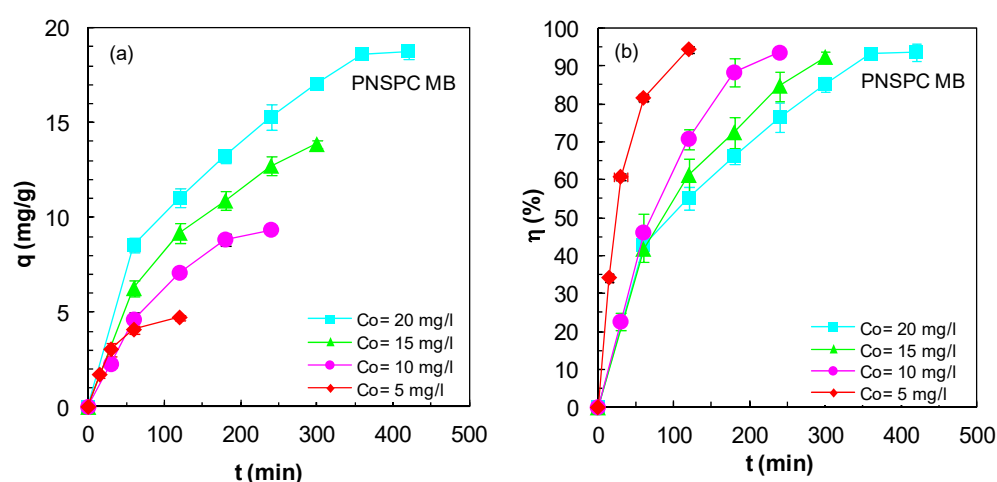


Figure 10. Color change in the samples solutions before and during adsorption of (a) methylene blue, from intense blue to colorless and (b) methyl orange, from intense orange to colorless.

3.2.3. Effect of the Initial Concentration of the Adsorbate

The impacts of the initial concentration of the adsorbate on the adsorption capacity and efficiency using solutions with initial concentrations of 5, 10, 15, and 20 mg/L of methylene blue or methyl orange on 1 g/L of adsorbent derived from pine nut shells and olive stones activated with H_3PO_4 (i.e., PNSPC and OSPC), are depicted in Figure 11. The

adsorption capacity was found to increase with the time to a maximum value which was similar for both dyes. Nevertheless, the adsorption capacity of methyl orange at equilibrium was slightly lower than that of methylene blue—mainly at low concentrations of the adsorbate. In particular, the time to equilibrium for methyl orange was 15% longer at the maximum concentration of adsorbate (20 mg/L) for PNSPC and 66% for OSPC. As the initial concentration of methylene blue increased from 5 to 20 mg/L, the adsorption capacity at equilibrium increased almost four times for PNSPC and OSPC, with the concentration gradient favorably affecting the diffusion of the adsorbate. In the case of methyl orange, the adsorption capacity increased by nearly five times for PNSPC and seven times for OSPC. The evolution of the adsorption capacity of PNSPC for both adsorbates is directly proportional to time, while the evolution of OSPC showed an increase that is more than proportional to time. Furthermore, upon comparing the adsorption capacities of the two adsorbents, it is evident that although their adsorption capacity and efficiency values are of the same order, those corresponding to the OSPC adsorbent were slightly higher than those corresponding to the PNSPC adsorbent, with equilibrium reached within shorter times for the former. The adsorption efficiency of PNSPC for methylene blue and methyl orange and that of OSPC for methyl orange increased with higher adsorbate concentration, while the performance of OSPC for MB hardly varied with concentration, achieving an adsorption efficiency of methylene blue close to 100% in both adsorbents. The adsorption efficiency of methyl orange was 20% lower than that for methylene blue, except for the concentration of 20 mg/L, at which practically the same efficiency was achieved. Although similar trends were observed for both adsorbents activated with NaOH, the adsorption capacity of the adsorbents activated with H_3PO_4 was around 5 times higher and the efficiency was almost double at an initial methylene blue concentration of 20 mg/L. The adsorption capacity and efficiency values obtained with commercial activated charcoal were similar to those obtained with these adsorbents, although both were achieved in a quarter of the time.



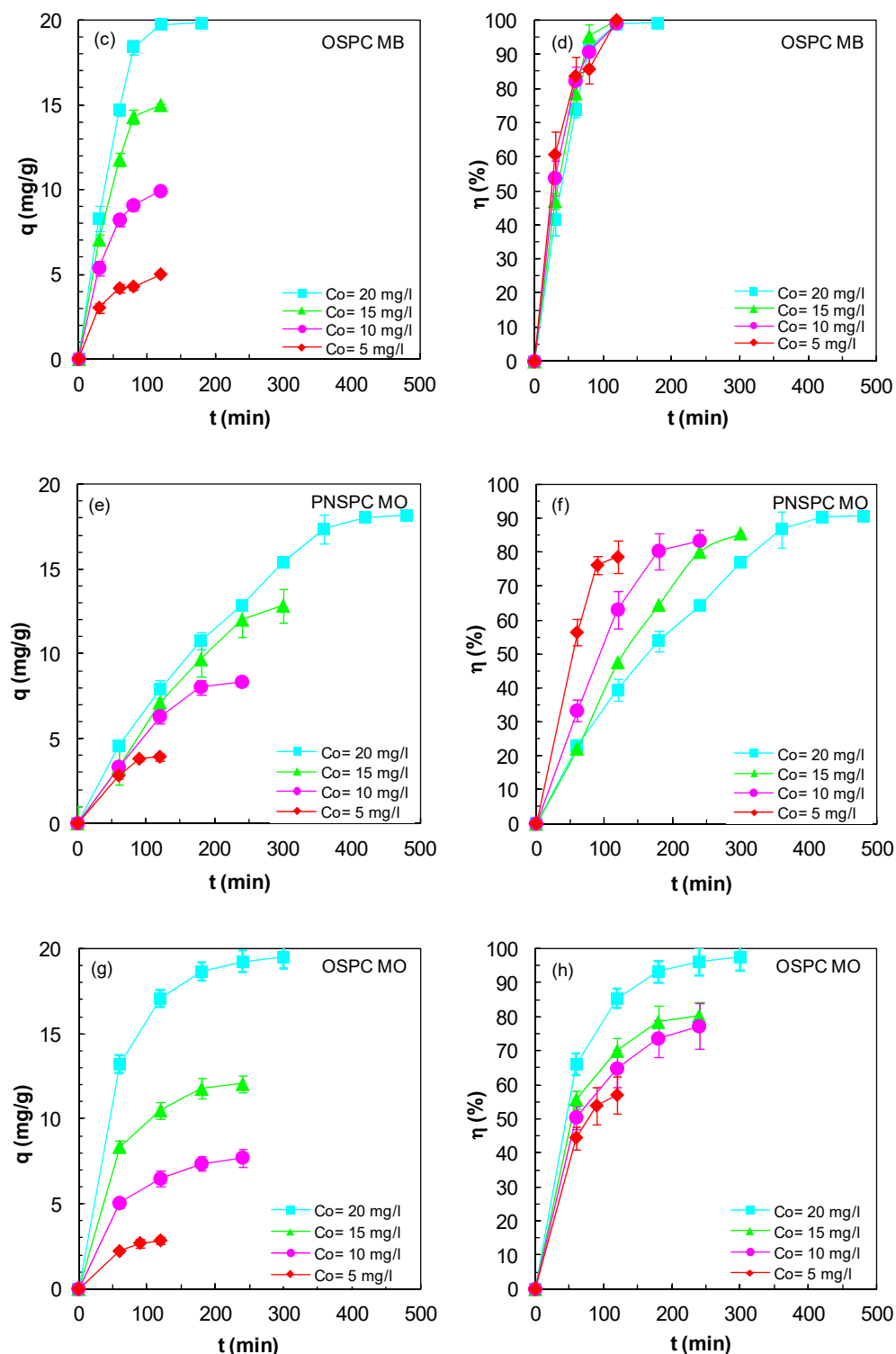


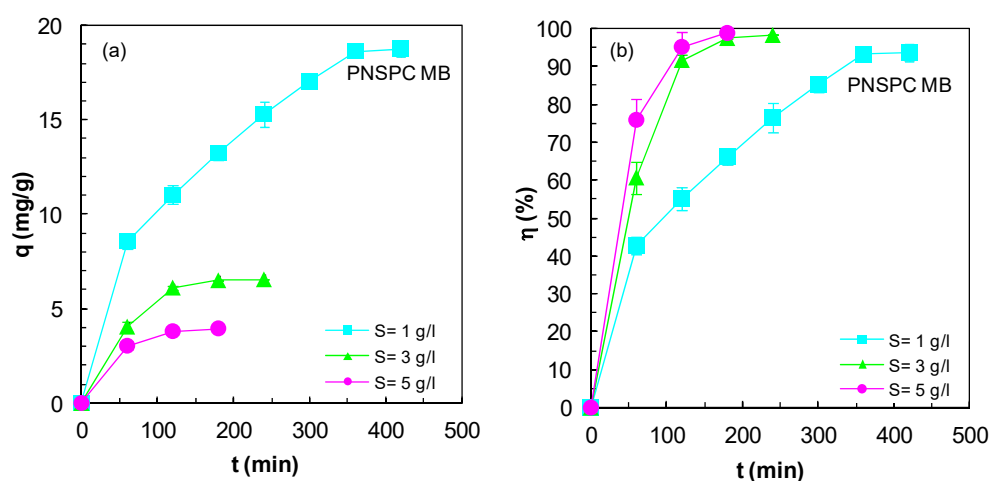
Figure 11. Time evolution of adsorption capacity and efficiency of methylene blue and methyl orange with the activated adsorbents by triplicate tests. $C_0 = 5, 10, 15,$ and 20 mg/L and $S = 1$ g/L. (a) Adsorption capacity of PNSPC for MB, (b) adsorption efficiency of PNSPC for MB, (c) adsorption capacity of OSPC for MB, (d) adsorption efficiency of OSPC for MB, (e) adsorption capacity of PNSPC for MO, (f) adsorption efficiency of PNSPC for MO, (g) adsorption capacity of OSPC for MO, (h) adsorption efficiency of OSPC for MO.

3.2.4. Effect of the Adsorbent Concentration

Figure 12 depicts the impacts of the concentration of adsorbent on adsorption capacity and efficiency using different amounts of activated adsorbents (1, 3, and 5 g/L PNSPC and OSPC) with solutions of methylene blue and methyl orange at a concentration of 20 mg/L. Equilibrium was reached in half the time when the adsorbent concentration was five times higher for both methylene blue and methyl orange. Additionally, the adsorption capacity at equilibrium decreased inversely to the amount of adsorbent; particularly increasing from 1 to 3 g/L, where the capacity was almost four times higher at 1 g/L compared with 5 g/L. This tendency can be attributed to the increase in the number of adsorption sites at higher adsorbent concentrations. The adsorption efficiency of methylene blue on both adsorbents activated with H_3PO_4 was nearly 100%, even with an only 1 g/L of adsorbent. The efficiency was nearly 100% at a concentration of 1 g/L with PNSPC and OSPC for methylene blue and for methyl orange with OSPC, and was around 90% with PNSPC for methyl orange. The increase in efficiency was lower, at 40%, with a steeper slope from 1 to 3 g/L and a slight variation from 3 to 5 g/L. Furthermore, the time to reach maximum efficiency for methylene blue was approximately half for OSPC (120 min) when compared with PNSPC (240 min). The time to maximum efficiency for methyl orange was reduced by 10% for OSPC compared with PNSPC.

This pattern was also observed for adsorbents activated with NaOH (i.e., PNSNC and OSNC), although with lower adsorption capacity and efficiency. The adsorption capacity and efficiency values obtained with commercial activated charcoal were similar to those of the other adsorbents, but were achieved in shorter times (i.e., 15, 18, and 20 min) with adsorbent concentrations of 5, 3, and 1 g/L, respectively.

The difference in the performance of bioadsorbents between MB and MO was primarily due to their chemical properties and the nature of their interaction with the adsorbent surface. The adsorption kinetics were slightly faster for MB than for MO, which is attributed to the higher affinity of the former for the adsorbent surface. At pH 7.3, the solution was above the point of zero charge of the activated carbons ($\text{pH}_{\text{pzc}} = 6.5\text{--}6.9$), rendering the adsorbent surface negatively charged. This determines the affinity for and kinetic behavior of the dyes based on their ionic nature. As a cationic dye, MB experiences strong electrostatic attraction toward the negatively charged activated carbon surface, facilitating rapid migration to and binding with active sites. Conversely, as an anionic dye, MO experiences repulsive forces and, thus, shows a lower affinity (mainly based on weaker π - π stacking or hydrophobic interactions, rather than ionic bonds). For the same reasons, the adsorption capacity was somewhat higher for MB compared with MO.



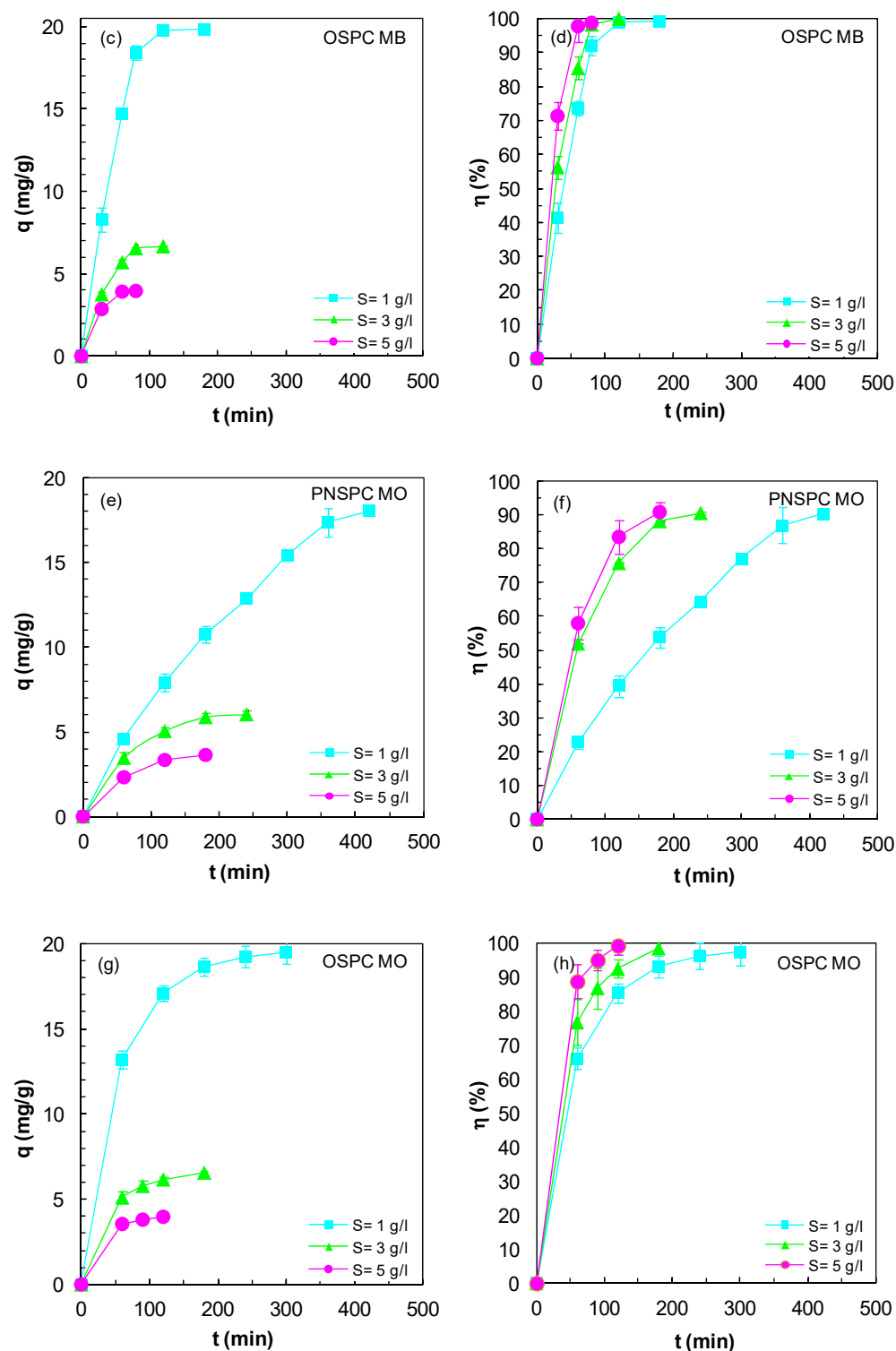


Figure 12. Time evolution of adsorption capacity and efficiency of methylene blue and methyl orange with the activated adsorbents by triplicate tests. $C_0 = 20$ mg/L and $S = 1, 3,$ and 5 g/L (a) adsorption capacity of PNSPC for MB, (b) adsorption efficiency of PNSPC for MB, (c) adsorption capacity of OSPC for MB, (d) adsorption efficiency of OSPC for MB, (e) adsorption capacity of PNSPC for MB, (f) adsorption efficiency of PNSPC for MB, (g) adsorption capacity of OSPC for MB, (h) adsorption efficiency of OSPC for MB.

To determine the maximum adsorption capacity of the adsorbents, an adsorption experiment was carried out with a solution of methylene blue and methyl orange at an

initial concentration of 50 mg/L and 0.1 g/L of the activated adsorbents PNSPC and OSPC. As can be observed from Figure 13, the adsorption capacity at equilibrium for the OSPC adsorbent with MB was 300 mg/L and with MO was 285 mg/L, while for PNSPC with MB was 240 mg/L and with MO was 229 mg/L.

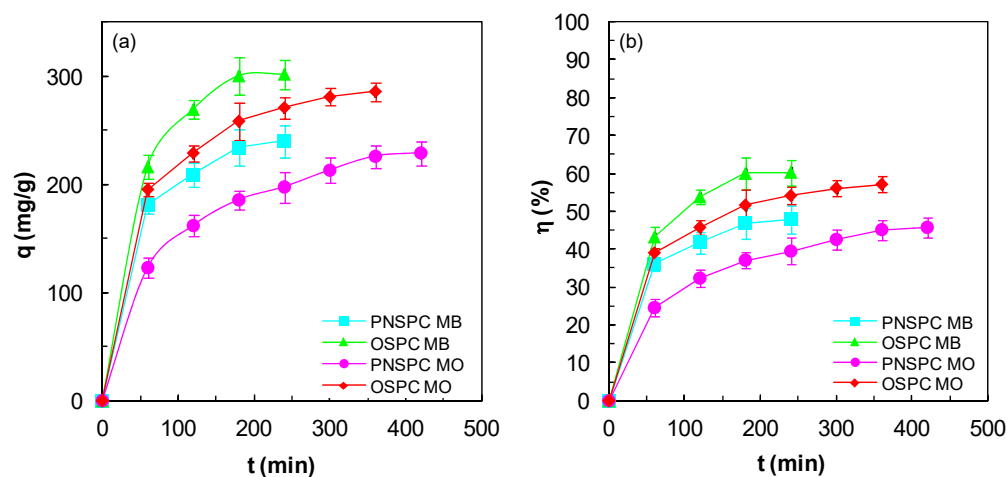


Figure 13. Time evolution of adsorption capacity and efficiency of methylene blue and methyl orange with the activated adsorbents. $C_0 = 50$ mg/L and $S = 0.1$ g/L (a) adsorption capacity, (b) adsorption efficiency.

The experimental methylene blue adsorption capacity values for the adsorbents were compared with similar results reported in other studies (Table 3). The adsorption capacity of methylene blue onto adsorbents derived from pine nut shells activated with H_3PO_4 was double that reported by Naushad et al. [71] for pine nut shells activated with NaOH under similar conditions (25 mg/L, $q = 8.97$ mg/g at 120 min), and three times that obtained by Kim et al. [38] for pine nut shells with thermal activation ($q = 6.09$ mg/g). Furthermore, it should be noted that both authors used larger quantities of adsorbent and Kim et al. (2025) [38] had a longer process time (24 h). Regarding the adsorbent from olive stones activated with H_3PO_4 ($q = 18.75$ mg/g), the values were almost four times higher than those reported by Hazzaa and Husein [73] with thermal activation ($q = 4.8$ mg/g), and 11% higher than those reported by Wafaa et al. [74] activated with H_3PO_4 ($q = 16.78$ mg/g), even with lower amounts of adsorbent. Adsorbents derived from pine nut shells and olive stones presented an adsorption capacity for methylene blue on the same order as those obtained by Kataya et al. [76] using an adsorbent derived from kitchen waste. Furthermore, both of their adsorption capacities for methyl orange were also similar to those obtained by Kataya et al. [76] using the adsorbent derived from kitchen waste.

Table 3. Previous studies on dyes adsorption.

Adsorbent	Dye	Activating Method	Operating Conditions	Adsorption Capacity (mg/g)	Adsorption Efficiency (%)	References
Pine nut shells	Methylene blue	NaOH	$C_0 = 25\text{--}200$ mg/L, $T = 25$ °C	8.97	92.54	[71]
Pine nut shells	Methylene blue	Thermal treatment	$C_0 = 0.3\text{--}9.6$ mg/L, $T = 15\text{--}35$ °C	6.09	67	[38]
Olive stones	Methylene blue	Washing	$C_0 = 20\text{--}140$ mg/L, $T = 25\text{--}45$ °C	44.5	93.65	[37]
Olive stones	Methylene blue	H_3PO_4/KOH	$C_0 = 10\text{--}70$ mg/L, $T = 23\text{--}32$ °C	16.78	-	[74]
Olive stones	Methylene blue	Thermal treatment	$C_0 = 50\text{--}120$ mg/L, $T = 25$ °C	4.8	96	[73]
Olive stones	Methylene blue	$ZnCl_2/H_3PO_4/KOH$	$C_0 = 100\text{--}300$ mg/L, $T = 30\text{--}50$ °C	294/70/125	39–65	[41]
Kitchen waste	Methylene blue	pyrolysis	$C_0 = 5\text{--}25$ mg/L, $T = 25$ °C	30.40	99.5	[76]

Waste tyre	Methylene blue	KOH + pyrolysis	Co = 30–271 mg/L, T = 5–35 °C	100–160	90	[77]
Data seeds	Methyl orange	H ₃ PO ₄ + pyrolysis	Co = 5–20 mg/L, T = 25 °C	7.57	15.3–99.82	[20]

3.2.5. Reutilization Capacity of the Adsorbents

The fact that the adsorption efficiency for methylene blue and methyl orange with both adsorbents derived from pine nut shells and olive stones activated with H₃PO₄ (PNSPC and OSNPC) reached almost 100% suggests that the adsorbents were not saturated, and thus have potential for reuse in consecutive cycles. The used adsorbents were filtrated and washed with deionized water for one hour to remove dye residues, three times consecutively. Finally, the adsorbents were dried at 105 °C for 24 h, then tested in a second cycle.

PNSPC and OSNPC adsorbents with a concentration of 1 g/L were utilized in 12 and 15 subsequent adsorption cycles, respectively, using solutions of methylene blue and methyl orange with an initial concentration of 20 mg/L each, resulting in a total mass loss of less than 0.5%. Figure 14 shows the adsorption efficiency with the number of adsorption cycles for the PNSPC adsorbent (Figure 14a) and OSNPC (Figure 14b) while Table 4 lists the cumulative adsorption capacity values. The observed adsorption efficiency was around 100% for the first four cycles and remained above 85% from the fifth cycle onward.

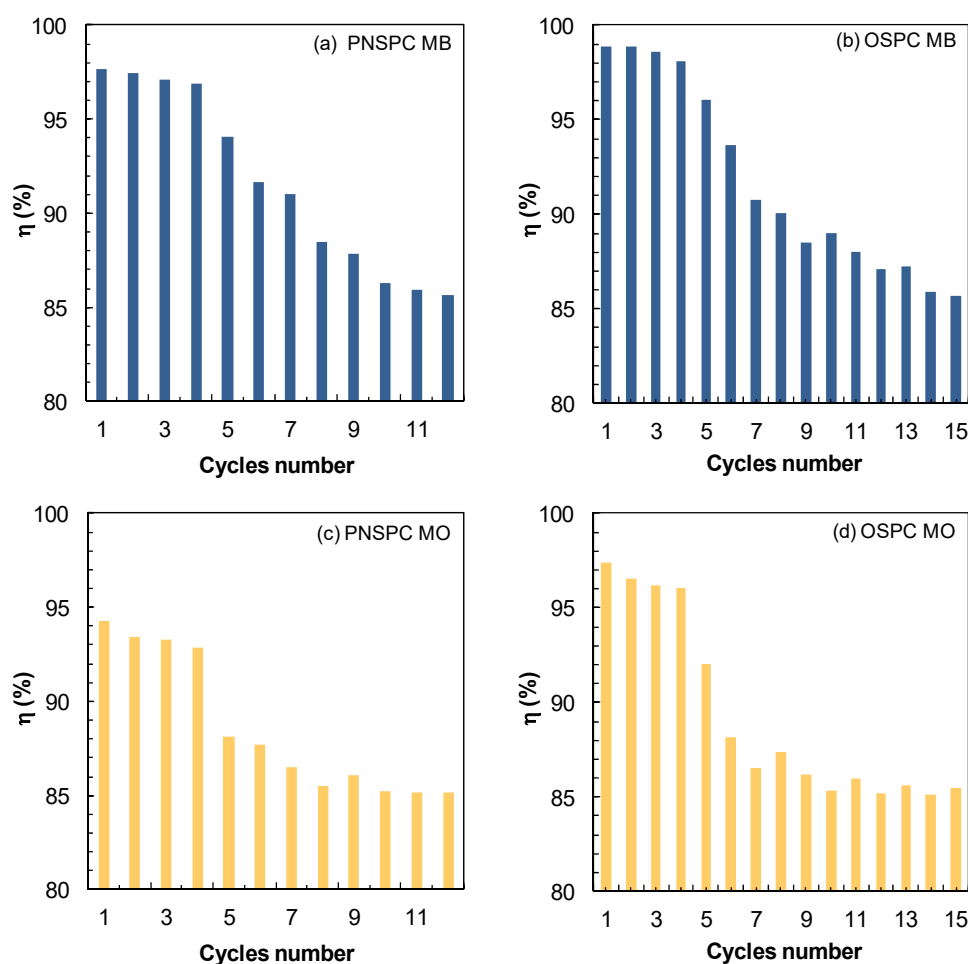


Figure 14. Adsorption efficiency evolution with subsequent adsorption cycles of methylene blue and methyl orange with $C_0 = 20$ mg/L on 1 g/L of (a) PNSPC adsorbent for MB, (b) OSNPC adsorbent for MB, (c) PNSPC adsorbent for MO, (d) OSNPC adsorbent for MO.

Table 4. Cumulative adsorption capacity with subsequent adsorption cycles of methylene blue and methyl orange with $C_0 = 20$ mg/L on 1 g/L of PNSPC and OSPC adsorbents.

Cycle Number	$q_{\text{cumulative}}$ (mg/g)			
	MB		MO	
	PNSPC	OSPC	PNSPC	OSPC
1	19.53	19.77	18.86	19.48
2	39.01	39.54	37.55	38.78
3	58.44	59.25	56.21	58.02
4	77.81	78.87	74.78	77.23
5	96.61	98.09	92.41	95.63
6	114.95	116.82	109.94	113.27
7	133.15	134.97	127.24	130.57
8	150.85	152.98	144.34	148.04
9	168.43	170.68	161.56	165.28
10	185.68	188.48	178.61	182.35
11	202.87	206.09	195.64	199.55
12	220	223.51	212.67	216.6
13		240.96		233.72
14		258.14		250.75
15		275.28		267.84

3.3. Adsorption Process Kinetic Modeling

The experimental adsorption capacity values were fitted to the pseudo-first order, pseudo-second order, intra-particle diffusion, and Elovich kinetics models detailed in Table 5. The kinetic parameters of the models were determined through a nonlinear regression analysis using the `fminsearch` command in MATLAB 2025b software, which minimizes the error between the experimental data and the predicted values.

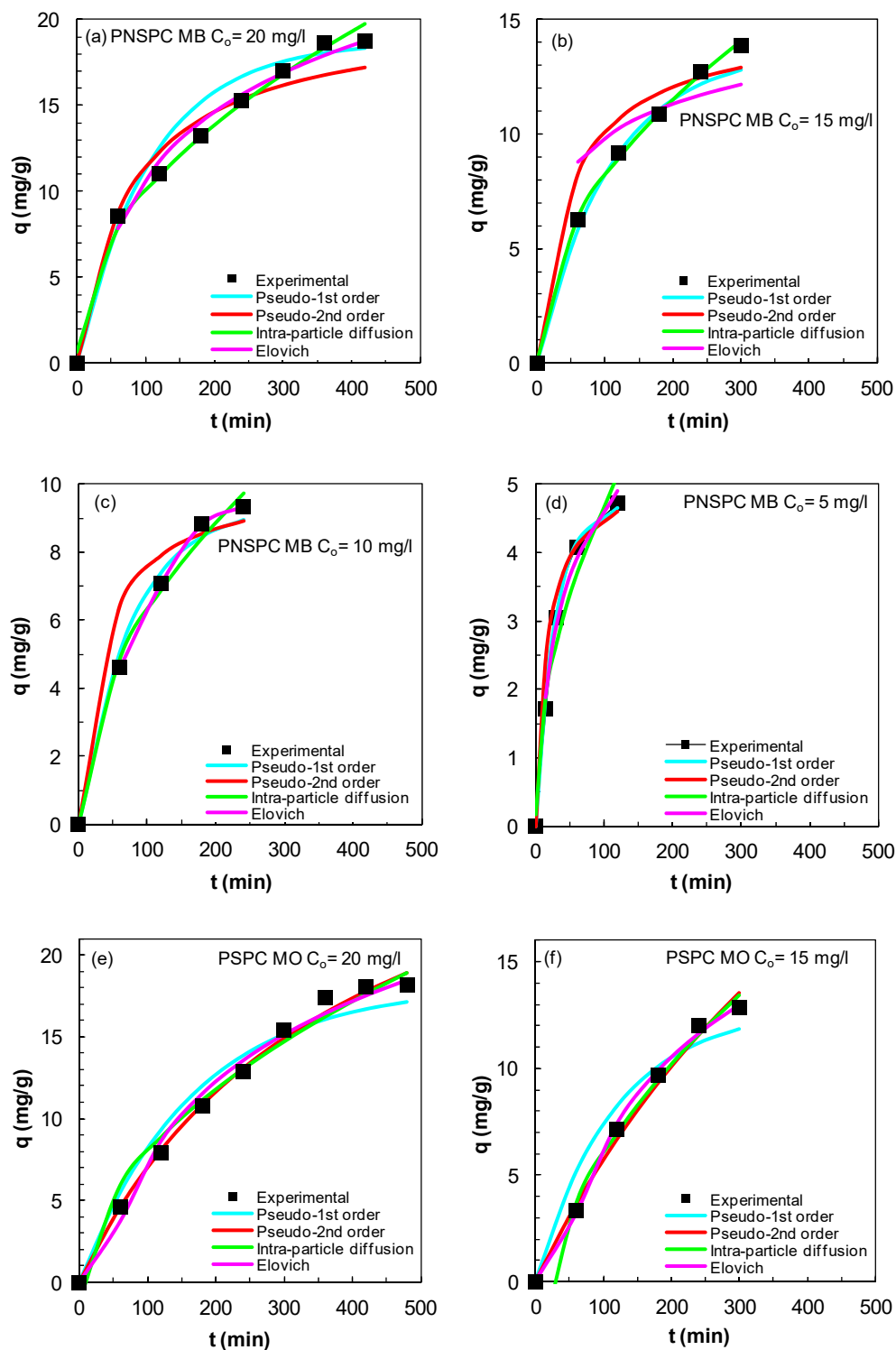
Table 5. Kinetic models equations.

Model	Model Equation	Equation
Pseudo-first order	$q_t = q_e (1 - e^{-k_1 t})$	(3)
Pseudo-second order	$q_t = \frac{1}{\frac{1}{k_2 q_{e \max}^2} + \frac{t}{q_{e \max}}}$	(4)
Intra-particle diffusion	$q_t = k_i t^{0.5} + I$	(5)
Elovich	$q_t = a + b \ln t$	(6)

Figures 15 and 16 show the fit of the experimental adsorption capacity values—namely for the adsorption of four solutions of methylene blue and methyl orange (at concentrations of 5, 10, 15, and 20 mg/L) onto the PNSPC and OSPC adsorbents—to the models obtained through nonlinear regression. The kinetic and statistical parameters are summarized in Tables 6 and 7.

Based on the statistical parameters in Tables 6 and 7, the adsorption capacity of the PNSPC and OSPC adsorbents for methylene blue and methyl orange can be accurately predicted using these models, this is because their coefficient of determination (R^2) is over 0.94, root mean square error (RMSE) is below 2, and residual sum of squares (RSS) is below 4. Tables 6 and 7 show that both k_1 and k_2 in the pseudo-first-order and pseudo-second-order models decrease as the initial concentration of adsorbate increases, which is in accordance with other studies [89]. Furthermore, according to the coefficients of determination (R^2), and the Akaike Information Criterion (AIC) for the pseu-

do-first-order kinetics compared with the corresponding pseudo-second-order kinetics along with the fact that the k_1/k_2 ratio is greater than 1, it can be concluded that the pseudo-first-order kinetics models for PNSPC and OSPC more closely describe the kinetic data. This suggests that their adsorption behavior is governed by physical adsorption (physisorption) or mechanisms controlled by the saturation of surface sites [90].



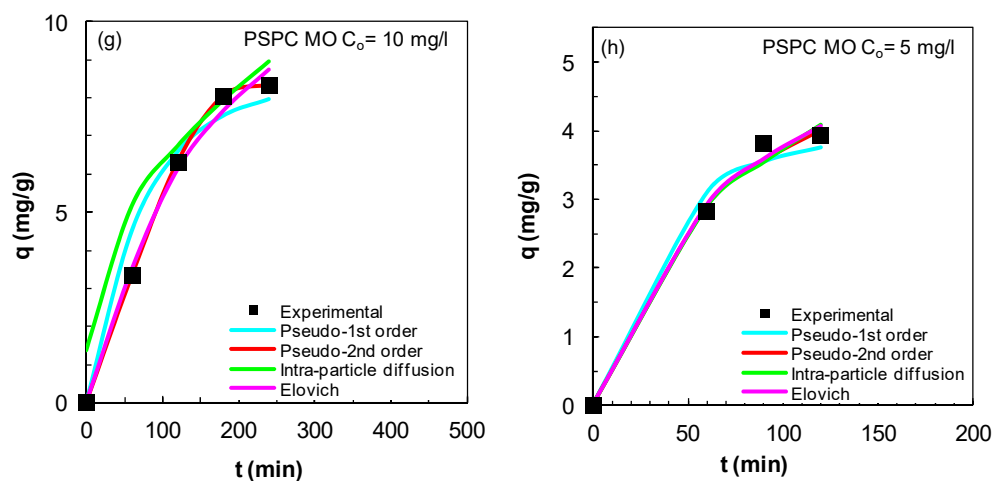
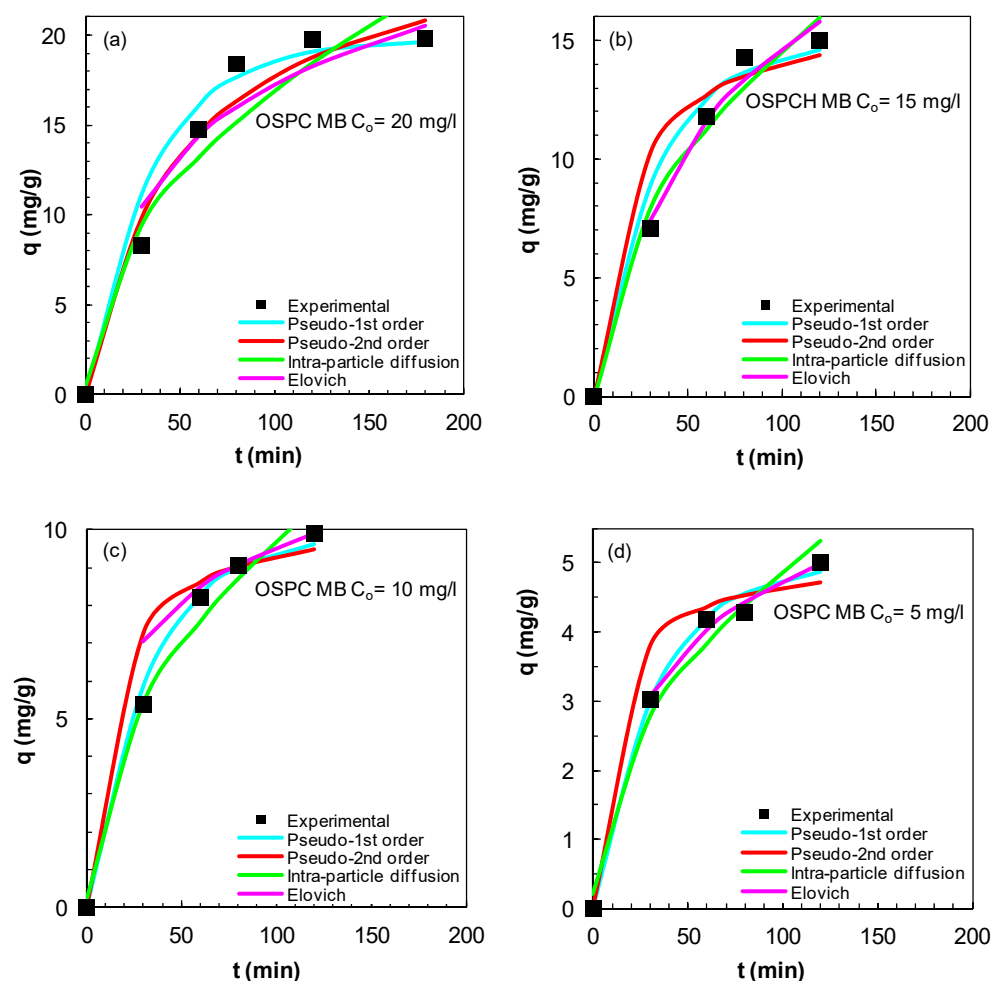


Figure 15. Time evolution of experimental values of adsorption capacity of PNSPC and calculated with the adsorption models $S = 1$ g/L. For MB (a) $C_0 = 20$ mg/L, (b) $C_0 = 15$ mg/L, (c) $C_0 = 10$ mg/L, (d) $C_0 = 5$ mg/L, for MO (e) $C_0 = 20$ mg/L, (f) $C_0 = 15$ mg/L, (g) $C_0 = 10$ mg/L, (h) $C_0 = 5$ mg/L.



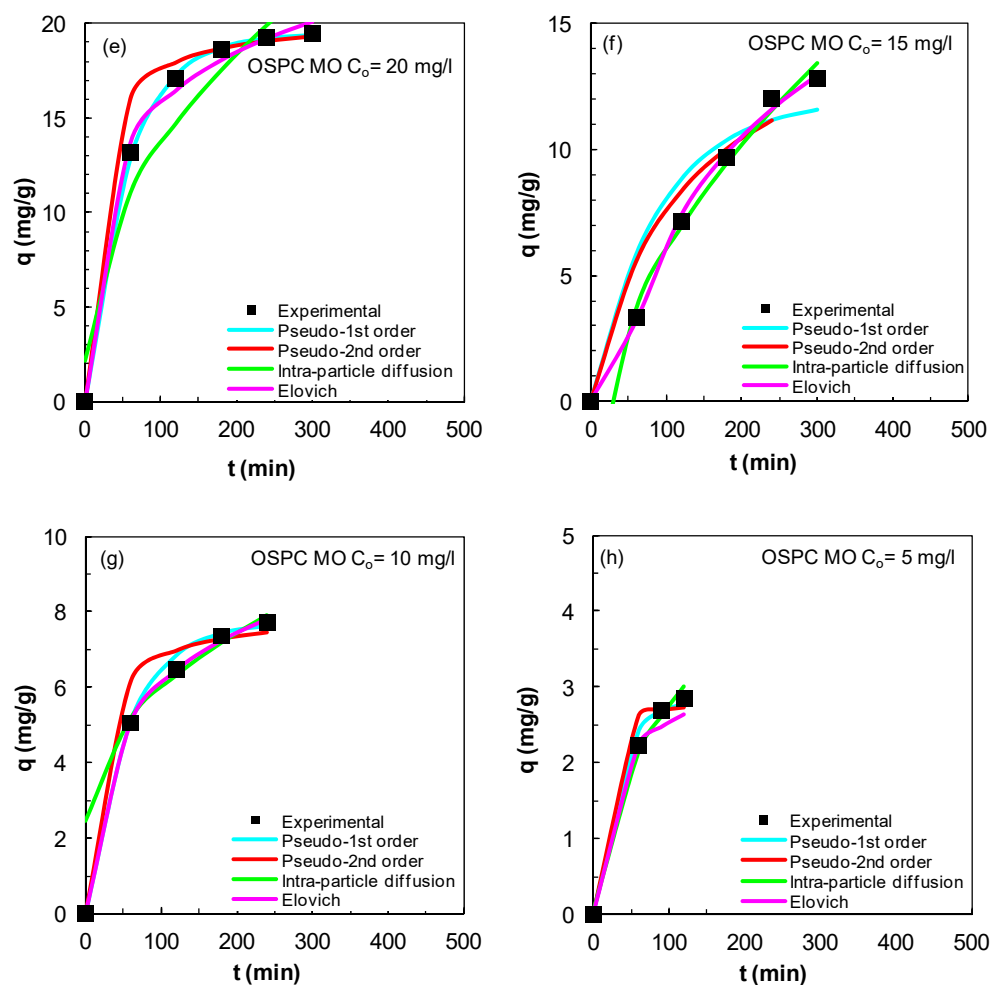


Figure 16. Time evolution of experimental values of adsorption capacity of OSPC and calculated with the adsorption models $S = 1$ g/L. For MB (a) $C_0 = 20$ mg/L, (b) $C_0 = 15$ mg/L, (c) $C_0 = 10$ mg/L, (d) $C_0 = 5$ mg/L, for MO (e) $C_0 = 20$ mg/L, (f) $C_0 = 15$ mg/L, (g) $C_0 = 10$ mg/L, (h) $C_0 = 5$ mg/L.

Table 6. Parameters and statistical indicators of the nonlinear regression of the adsorption kinetics models for adsorption of methylene blue on PNSPC and OSPC adsorbents.

Adsorbent		C_0 (mg/L)			
		5	10	15	20
PNSPC	q_{exp} (mg/g)	4.72	9.35	13.86	18.13
	Pseudo-1st order				
	q_{cal} (mg/g)	4.65	8.94	13.17	18.75
	k_1 (min^{-1})	0.035	0.013	0.010	0.009
	R^2	0.998	0.995	0.995	0.987
	RMSE	0.12	0.39	0.49	1.14
	RSS	0.01	0.15	0.24	1.30
	AIC	-21.97	-11.13	-13.18	-9.78
	Pseudo-2nd order				
	q_{cal} (mg/g)	5.24	10.22	15.04	17.20
	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.011	0.002	0.001	0.0006
	R^2	0.982	0.969	0.976	0.993
	RMSE	0.42	1.03	1.23	1.68
	RSS	0.18	1.06	1.51	2.81
	AIC	-10.40	-3.31	-3.99	-4.39

	k_1/k_2	3.182	6.500	10.000	15.333
Intra-particle diffusion					
q_{cal} (mg/g)		5.12	9.72	14.08	18.70
k_i (mg/g/min ^{-0.5})		0.45	0.73	0.081	0.933
I (mg/g)		0.17	-0.009	0.06	0.369
R ²		0.980	0.995	0.999	0.998
RMSE		0.36	0.32	0.16	0.49
RSS		0.13	0.10	0.03	0.24
AIC		-9.71	-10.76	-15.57	-7.25
Elovich					
q_{cal} (mg/g)		4.89	9.56	12.18	17.71
a (mg/g)		-2.05	-9.83	0.20	-15.18
b (mg/g)		1.45	3.54	2.1	5.61
R ²		0.980	0.995	0.999	0.978
RMSE		0.17	0.18	1.51	0.57
RSS		0.03	0.03	2.28	0.33
AIC		-15.57	-15.57	1.75	-5.98
OSPC	q_{exp} (mg/g)	5.0	9.91	15.00	19.76
Pseudo-1st order					
q_{cal} (mg/g)		4.86	9.64	14.59	19.07
k_1 (min ⁻¹)		0.03	0.03	0.03	0.028
R ²		0.997	0.997	0.987	0.982
RMSE		0.14	0.26	1.07	1.69
RSS		0.01	0.07	1.14	2.87
AIC		-21.97	-14.18	-3.02	-0.78
Pseudo-2nd order					
q_{cal} (mg/g)		5.13	10.55	16.61	20.77
k_2 (g mg ⁻¹ min ⁻¹)		0.018	0.007	0.003	7.4×10^{-4}
R ²		0.982	0.974	0.964	0.981
RMSE		0.38	0.89	1.77	1.28
RSS		0.14	0.79	3.13	1.61
AIC		-11.41	-4.49	1.02	-3.67
k_1/k_2		1.667	4.286	10.000	37.838
Intra-particle diffusion					
q_{cal} (mg/g)		0.22	10.62	15.96	20.53
k_i (mg/g/min ^{-0.5})		5.31	0.94	-0.06	1.91
I (mg/g)		0.22	0.22	1.46	-0.45
R ²		0.989	0.991	0.988	0.987
RMSE		0.27	0.47	0.95	1.30
RSS		0.07	0.22	0.91	1.69
AIC		-12.18	-7.60	-1.92	0.55
Elovich					
q_{cal} (mg/g)		4.98	9.91	15.77	20.66
a (mg/g)		-1.62	-0.003	-13.06	-20.7
b (mg/g)		1.38	2.07	6.02	8.64
R ²		0.988	0.988	0.978	0.984
RMSE		0.11	0.84	0.63	0.79
RSS		0.01	0.73	0.42	0.63
AIC		-19.97	-2.80	-5.02	-3.39

Table 7. Parameters and statistical indicators of the nonlinear regression of the adsorption kinetics models for adsorption of methyl orange on PNSPC and OSPC adsorbents.

Adsorbent		C _o (mg/L)			
		5	10	15	20
PNSPC	q _{exp} (mg/g)	3.93	8.34	12.84	18.14
Pseudo-1st order					
	q _{cal} (mg/g)	3.93	8.23	12.37	18.05
	k ₁ (min ⁻¹)	0.026	0.013	0.008	0.011
	R ²	0.992	0.983	0.981	0.988
	RMSE	0.210	0.612	1.021	0.780
	RSS	0.044	0.375	2.050	0.610
	AIC	-16.01	-10.95	-8.47	-22.24
Pseudo-2nd order					
	q _{cal} (mg/g)	6.48	16.83	43.67	34.24
	k ₂ (g mg ⁻¹ min ⁻¹)	0.002	2.60 × 10 ⁻⁴	3.44 × 10 ⁻⁵	7.52 × 10 ⁻⁵
	R ²	0.996	0.994	0.995	0.997
	RMSE	0.137	0.353	0.361	0.421
	RSS	0.019	0.125	0.130	0.177
	AIC	-19.43	16.45	-20.98	-33.34
	k ₁ /k ₂	13.00	50.00	232.56	146.27
Intra-particle diffusion					
	q _{cal} (mg/g)	4.09	9.42	13.42	18.84
	k _i (mg/g/min ^{-0.5})	0.373	0.491	1.021	0.916
	I (mg/g)	0.011	1.366	-4.262	-1.176
	R ²	0.995	0.994	0.979	0.990
	RMSE	0.160	1.081	1.776	0.873
	RSS	0.026	1.168	3.156	0.763
	AIC	-18.21	-5.27	-1.86	-20.21
Elovich					
	q _{cal} (mg/g)	4.06	8.74	12.96	18.19
	a (mg/g)	-3.869	-11.960	-21.723	-25.361
	b (mg/g)	1.656	3.777	6.081	7.103
	R ²	0.947	0.988	0.997	0.994
	RMSE	0.160	0.306	0.246	0.679
	RSS	0.026	0.094	0.060	0.461
	AIC	-18.21	-17.28	-25.60	-24.74
OSPC	q _{exp} (mg/g)	2.85	7.72	12.84	19.48
Pseudo-1st order					
	q _{cal} (mg/g)	2.78	7.72	11.57	19.39
	k ₁ (min ⁻¹)	0.031	0.018	0.011	0.018
	R ²	0.996	0.998	0.962	0.999
	RMSE	0.101	0.186	1.534	0.174
	RSS	0.010	0.034	2.35	0.03
	AIC	-21.38	-22.87	-3.61	-29.70
Pseudo-2nd order					
	q _{cal} (mg/g)	2.85	8.02	13.43	20.32
	k ₂ (g mg ⁻¹ min ⁻¹)	0.062	0.007	4.80 × 10 ⁻⁴	0.003
	R ²	0.986	0.984	0.975	0.987
	RMSE	0.203	0.555	1.258	1.199
	RSS	0.041	0.308	1.581	1.438
	AIC	-22.01	-11.94	-6.00	-6.82
	k ₁ /k ₂	0.50	2.57	22.91	6.00

Intra-particle diffusion				
q_{cal} (mg/g)	2.99	7.91	13.43	22.06
k_i (mg/g/min ^{-0.5})	0.270	0.352	1.021	1.148
I (mg/g)	0.039	2.459	-4.262	2.180
R^2	0.996	0.984	0.979	0.959
RMSE	0.101	1.110	0.392	1.907
RSS	0.010	1.233	0.154	3.638
AIC	-28.99	-5.00	-19.99	0.998
Elovich				
q_{cal} (mg/g)	4.78	7.82	12.96	20.12
a (mg/g)	-0.139	-3.004	-21.723	-2.571
b (mg/g)	0.582	1.975	6.081	3.978
R^2	0.983	0.997	0.999	0.998
RMSE	0.149	0.069	0.224	0.472
RSS	0.022	0.005	0.05	0.223
AIC	-25.07	-32.71	-26.70	-17.75

3.4. Adsorption Isotherms

The adsorption isotherm represents the nonlinear dynamic equilibrium of the adsorption–desorption process between the adsorbate adsorbed on the adsorbent, q_e , and the concentration of the adsorbate remaining in the solution, C_e , at equilibrium and constant temperature. The isotherm models of adsorption–desorption provide information on the behavior of the adsorbent–adsorbate system and enable prediction of how to improve the adsorption capacity and/or optimize the adsorbent–adsorbate relationship. The most used models in the literature to describe adsorption isotherms are the Langmuir, Freundlich, and Sips models (Table 8).

Table 8. Isotherm models.

Model	Model Equation	Equation
Langmuir	$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e}$	(7)
Freundlich	$q_e = K_F C_e^{1/n}$	(8)
Sips	$\frac{q_e}{q_m} = \frac{(K_S C_e)^{1/n}}{1 + (K_S C_e)^{1/n}}$	(9)

The equilibrium data for the adsorption of three solutions of methylene blue and methyl orange (initial concentration 20 mg/L) onto different amounts of PNSPC and OSPC adsorbents ($S = 1, 3$, and 5 g/L) were fitted to various isotherm models using nonlinear regression analysis with the `fminsearch` command in MATLAB 2025b software. This method minimizes the error between the experimental and the predicted data, allowing for the determination of isotherm parameters.

Figure 17 illustrates the experimental isotherm of methylene blue and methyl orange on the PNSPC and OSPC adsorbents along with the nonlinear regression models. Table 9 displays the parameters of the models, as well as statistical indicators. Comparing the statistical parameters, the Freundlich model appears to provide the best fit for the PNSPC adsorption isotherm; meanwhile, for OSPC the Freundlich and Langmuir isotherm models fit the data well, although the Langmuir model provides the best fit.

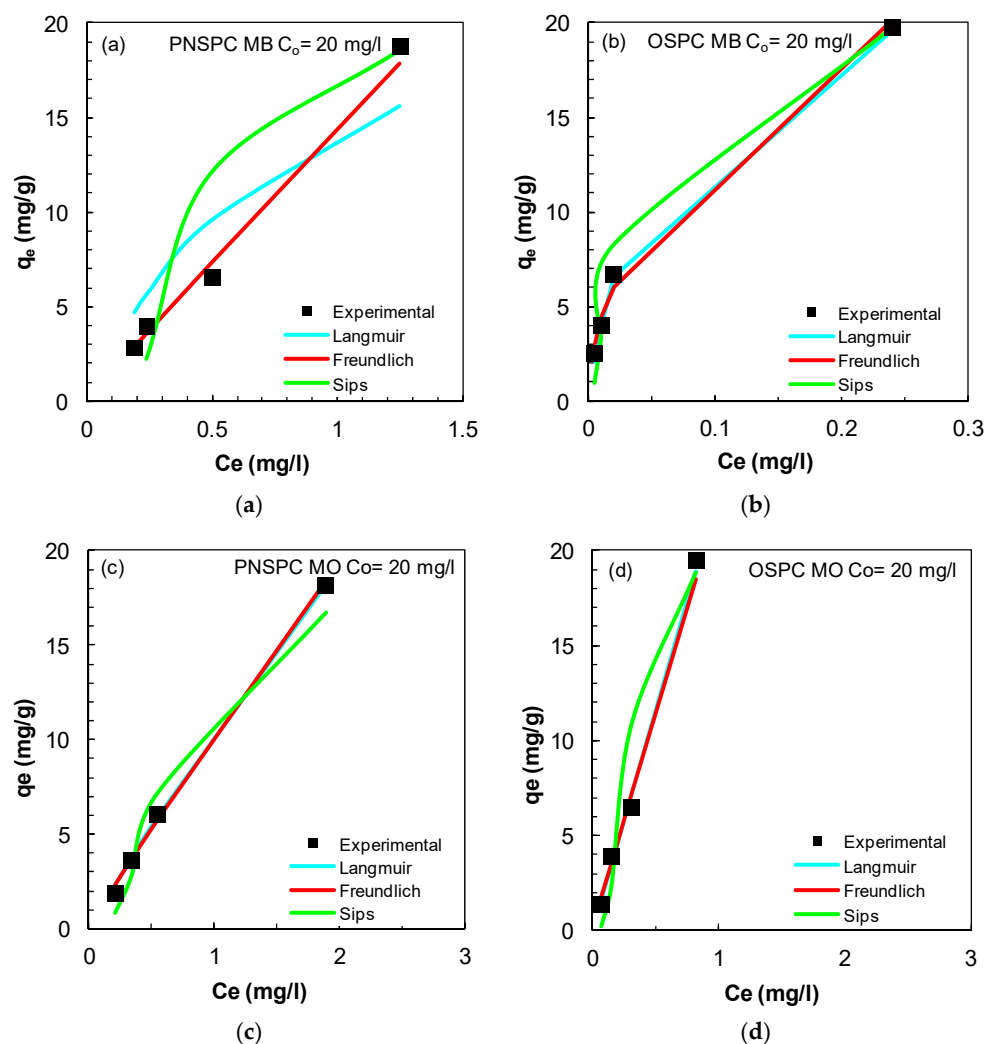


Figure 17. Experimental isotherm values (points) and values calculated by the isotherm models for adsorption of methylene blue and methyl orange ($C_0 = 20 \text{ mg/L}$, $S = 1, 3$, and 5 g/L) on (a) PNSPC for MB, and (b) OSPC for MB, (c) PNSPC for MO, and (d) OSPC for MO.

Table 9. Parameters and statistical indicators of the nonlinear regression of the isotherm models for adsorption of methylene blue and methyl orange on PNSPC and OSPC adsorbents.

Adsorbent	Dye	Langmuir							Freundlich					Sips						
		$q_{\max}$ (mg/g)	K_L (l/mg)	R^2	RMSE	RSS	AIC	K_F ($\text{mg}^{1-1/n}$ $\text{g}^{-1}\text{L}^{1/n}$)	n	R^2	RMSE	RSS	AIC	$q_{\max}$ (mg/g)	K_S (l/mg)	n	R^2	RMSE	RSS	AIC
PNSPC	Methylene blue	15.6	27	0.974	2.69	7.25	6.65	14.4	1.03	0.996	0.71	0.50	0.64	18.57	2.35	0.29	0.890	3.36	11.3	9.98
OSPC	Methylene blue	23.9	199	0.999	0.15	0.02	-10.70	40.3	2.06	0.998	0.47	0.22	-1.84	19.74	41.56	0.53	0.990	1.03	1.07	2.89
PNSPC	Methyl orange	126.58	0.089	0.999	0.10	0.01	-12.80	10.15	1.07	0.999	0.21	0.04	-6.63	18.14	1.569	0.368	0.987	1.17	1.37	3.67
OSPC	Methyl orange	769.23	0.031	0.996	0.610	0.372	-2.26	22.37	1.04	0.996	0.76	0.57	1.03	19.48	3.489	0.328	0.925	2.72	7.41	8.71

4. Conclusions

Four activated biocarbons were prepared from two widely available lignocellulosic biomass wastes (pine nut shells, PNS; and olive stones, OS), each subjected to two chemical pretreatments (with H_3PO_4 or NaOH) before being subjected to the same thermal activation treatment. These waste-derived adsorbents were prepared via a low-cost and sustainable process, and could contribute to a zero-waste and circular economy. The performance of the adsorbents regarding the removal of two reference dyes (methylene blue (MB) and methyl orange (MO)) from water was evaluated at the lab-scale, performed at the optimal pH according to their corresponding pH_{Pzc} values. The characteristics of the obtained adsorbents were evaluated through N_2 adsorption–desorption isotherms, FTIR and Raman spectroscopic analysis, and pH_{Pzc} determination. The adsorbents pretreated with phosphoric acid (PNSPC and OSPC) exhibited higher adsorption capacities and efficiencies than those activated with sodium hydroxide (PNSNC and OSNC). In particular, the OSPC adsorbent showed the highest adsorption capacity for both dyes (about 300 mg/g for MB and 285 mg/g for MO), even higher than that corresponding to PNSPC (240 mg/g for MB and 229 mg/g for MO), with adsorption efficiencies of around 100%, and an adsorption capacity comparable with that of the reference activated charcoal. All kinetic models showed a good fit according to the regression parameters. Nevertheless, the pseudo-first-order model was found to best describe the experimental data regarding the adsorption capacities of these adsorbents. Based on the statistical analysis, Langmuir and Freundlich models fit the adsorption isotherm data for OSPC well, with the Langmuir model being the one that best described the data, while the Freundlich model was a better fit for PNSPC.

The good performance observed for the H_3PO_4 -pretreated adsorbents (i.e., PNSPC and OSPC) was supported by the characterization techniques applied. The phosphoric acid-activated adsorbents exhibited a higher BET surface area, with OSPC showing the highest value (1535 m^2/g)—66% higher than that of commercial charcoal and almost eight times better than that of the adsorbent with the lowest surface area (PNSNC; 192 m^2/g). Furthermore, the total pore volume of OSPC was almost five times greater than that of PNSPC, and almost 30% greater than that of commercial charcoal.

The FTIR spectra showed that the H_3PO_4 -activated adsorbents had a common aromatic carbon backbone and stronger, broader peaks in the 1000–1450 cm^{-1} region—which is characteristic of a higher concentration of oxygen-containing functional groups (e.g., C–O, P–O–C bonds)—than the NaOH -activated adsorbents. The OSPC adsorbent showed the highest concentration of oxygen functional groups. The defect density, which is determined from the ratio of band intensities in Raman spectra, showed that the adsorbents derived from olive stones (OSPC and OSNC; I_D/I_G 0.801 and 0.702, respectively) exhibited greater disorder and carbonization defects than those derived from pine nut shells (PNSPC and PNSNC; I_D/I_G 0.684 and 0.617, respectively). Furthermore, the use of H_3PO_4 as an activating agent led to the production of a higher concentration of structural defects and more amorphous carbon regions when compared with NaOH . Bioadsorbents PNSPC and OSPC showed the best balance between aromaticity and defect density. Further considering the phosphoric acid-activated adsorbents (OSPC and PNSPC), an increase in their dosage from 1 to 5 g/L resulted in a significant decrease in the MB adsorption time (35% and 60%, respectively) with an adsorption efficiency close to 100%. At pH 3.5, the PNSPC and OSPC adsorbents exhibited MO adsorption efficiencies of 93.5% and 99.1%, respectively—values similar to those obtained for MB at pH 7.3: 91.2% with PNSPC and 97.9% with OSPC. For both bioadsorbents, the difference of the adsorption performance of MB and MO relied on their chemical properties and the nature of their electrostatic interactions between the dye molecules and the adsorbent surface, especially for MB as a cationic dye. At neutral or basic pH, there is a strong electrostatic attraction between the positively charged MB cations and the negatively

charged activated carbon surface, which makes the adsorption process spontaneous and highly efficient. Nevertheless, the negatively charged MO anions have a repulsive electrostatic force with the negatively charged carbon surface at neutral or basic pH, such that the adsorption is more favorable at acidic pH. The practical use of H₃PO₄-activated adsorbents was further experimentally determined through consecutive adsorption–desorption cycles (15 and 12 cycles for OSNPC and PNSPC, respectively). Regeneration of the solids in each cycle was carried out via thorough filtration, washing three consecutive times, and drying, with a total adsorbent mass loss of less than 0.5%. The adsorption efficiency remained at approximately 100% for the first four cycles and above 85% from the fifth cycle onward. Therefore, the OSNPC and PNSPC adsorbents could be applicable at the industrial level for the removal of emerging contaminants in urban wastewater treatment plants.

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Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

1/n	factor of heterogeneity of the Freundlich isotherm model (-)
a	adsorption constant of the Elovich kinetic model (mg g ⁻¹)
b	initial rate of adsorption of the Elovich kinetic model (mg g ⁻¹)
C _e , C ₀ , C	concentration of the adsorbate at the equilibrium, initial concentration of the adsorbate and concentration of the adsorbate at the time t, respectively (mg l ⁻¹)
I	value of the thickness of the boundary layer (mg g ⁻¹)
K _F	adsorbent–adsorbate equilibrium constant of the Freundlich isotherm model (mg ^{1-1/n} g ⁻¹ L ^{1/n})
K _L	adsorbent–adsorbate equilibrium constant of the Langmuir isotherm model (l mg ⁻¹)
K _S	adsorbent–adsorbate equilibrium constant of the Sips isotherm model (l mg ⁻¹)
k ₁	equilibrium constant of the pseudo-first-order kinetic adsorption model (min ⁻¹)
k ₂	equilibrium constant of the pseudo-second-order kinetic model (g mg ⁻¹ min ⁻¹)
k _i	equilibrium constant of the intra-particle diffusion kinetic model (mg g ⁻¹ /min ^{-0.5})
MB	methylene blue [‡]
MO	methyl orange
q, q _m , q _e , q _t	adsorption capacity, maximum adsorption capacity, adsorption capacities at the equilibrium and at any time, respectively (mg g ⁻¹)
S	the mass of the adsorbent (g)
V	volume of the solution (mL)
Greek Letters	
η	adsorption efficiency (%)

Abbreviations

The following abbreviations are used in this manuscript:

MB	methylene blue
MO	methyl orange
OS	olive stones
OSNC	olive stones activated with NaOH and carbonized
OSPC	olive stones activated with H ₃ PO ₄ and carbonized
PNS	pine nut shells
PNSNC	pine nut shells activated with NaOH and carbonized
PNSPC	pine nut shells activated with H ₃ PO ₄ and carbonized

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