

Adsorption of an anionic dye on a novel low-cost mesoporous adsorbent: kinetic, thermodynamic and isotherm studies

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Abstract. Our activated carbon was prepared successfully using phosphoric acid as an activated agent. The activated carbon was characterized by Scanning Electron Micrograph (SEM), Brunauer-Emmett-Teller (BET), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The aim of our study is to evaluate the adsorption capacity of Methyl Orange (MO) on *Ziziphus lotus* activated carbon. Adsorption isotherms were studied according to Langmuir and Freundlich Model, and adsorption kinetics according to pseudo-first and second-order. Results show that the maximum adsorption was reached in the first 10min at ambient temperature with a yield of 96.31%. The Langmuir isotherm shows a correlation coefficient of 99.4 % higher than the Freundlich model and the adsorption kinetic model follow a pseudo-second-order with a maximum adsorption capacity of 769.23 mg/g. FTIR and X-Ray spectroscopy indicate that our activated carbon has an amorphous structure with the presence of functional groups, where BET analysis revealed a high surface area of 553 mg/g, which facilitate the adsorption process.

Keywords: Adsorption, Methyl Orange, *Ziziphus lotus*.

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1. Introduction

Numerous industries such as textile, leather, paper, rubber, paint and a plastic used in their application extensive compounds lead to discharges toxic colored effluent, contaminates surface and groundwater. Textile wastewater, generally, contains a big amount of pollutants materials like colored materials or dyes, organic compounds and heavy metals ions, these colored materials can affect the physicochemical and the biological properties of the sea, drinking water and globally the ecosystem. In addition to the undesirable colors of textile effluents, some dyes may degrade to produce carcinogens and toxic products [1]. Methyl orange (MO), an anionic dye belongs to the azo and the more toxic group of dyes. MO has been widely used in textile, paper, plastics, rubber, cosmetics, printing, dye manufacturing and pharmaceutical industries [2].

The removal of industrial pollutants containing the aromatic band from water has become increasingly necessary in recent years and determining processes to achieve this is the focus of much scientific research. Researchers are indulging their interest in the wastewater treatment by various processes such as precipitation, ion exchange, reverse osmosis, and adsorption. Among these methods, Adsorption process is recognized as one of the most promising and effective approaches in wastewater treatment because of its low-cost ease of operation and high-efficiency [3]. There are currently a number of adsorbents including clay minerals, agricultural solid wastes are economical adsorbents, but they suffer from limited adsorption capacities of color removal.

This study highlights the adsorption activity of Methyl Orange (MO) from an aqueous solution onto *Ziziphus Lotus* activated carbon. MO is stable, shows solubility in water and low biodegradability; hence it is difficult to remove from aqueous solutions by common water purification or treatment methods [4], several factors affected the biosorption were studied in this work as pH, adsorbent dose, contact time and temperature, to deduce the adsorption thermodynamic and kinetic behavior process. The experimental results revealed a high adsorption capacity of MO adsorption on our sorbent.

2. Material and methods

2.1. Material and reagents:

To test the capacity of *Ziziphus Lotus* sorption, diverse laboratories materials were used in this work: UV visible spectroscopy, multi-parameter Consort C3040 was used for pH measurements, the pH values were adjusted using HCl (0.1N) or NaOH (0.1N) buffer solutions, multi agitator. Methyl orange (MO) ($C_{14}H_{14}N_3NaO_3S$), obtained from Sigma Aldrich, with a molecular weight of 327.32 g/mol and λ max of 464 nm. Solutions were prepared by dilution with distilled water from the stock solution of MO with the initial concentration of 1000 ppm to reach the desired concentration.

2.2 Characterization of the activated carbon:

Ziziphus leaves are very abundant in Morocco and not valorized were collected from Settat- Casablanca, Morocco, washed several times to eliminate the impurities and then activated with the phosphoric acid to obtain the activated carbon. The physicochemical properties of our activated carbon were determined by several analysis methods such as the (BET) Surface Area Analysis using a micrometric machine model 3 FLEX 3500, the surface morphology and the elemental composition was executed by SEM and Energy

Dispersive X-Ray (EDX) using an FEI Quanta 450 FEG Environmental Scanning Electron Microscope (ESEM), the X-ray diffraction using a D2 PHASER-BREKUR and FT-IR spectroscopy analyses were performed using a Transform Spectrometer (SHIMADZU FTIR-8400S).

2.3 Adsorption experiments:

The adsorption of Methyl Orange on the activated carbon was investigated as an effect of pH, initial dye concentration, contact time, and temperature. Adsorption experiments were reached after stirring 100mL of MO solution with different adsorbent doses and contact time at ambient temperature and agitation speed of 300 Rpm. The suspensions were collected then centrifuged and MO equilibrium concentrations were determined by spectrophotometry UV-VIS at 464 nm. The amount of MO adsorbed at equilibrium noted q_e in $\text{mg}\cdot\text{g}^{-1}$ and R the yield of adsorption in (%), respectively, were calculated by the following equations (Eq.1 and Eq.2):

$$q_e = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$R (\%) = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (2)$$

Where:

- C_0 : the initial dye concentration ($\text{mg}\cdot\text{L}^{-1}$),
- C_t : the equilibrium dye concentration ($\text{mg}\cdot\text{L}^{-1}$),
- V: the volume of the solution,
- m: the mass of the adsorbent (g).

Kinetic experiments were carried out by agitating 100 ml of MO solution at a constant dye concentration of 100ppm with 60 mg the activated carbon at fixed agitation speed, ambient temperature and pH = 2. Agitation was made from 5 to 120 min. Adsorption isotherm was obtained by varying the initial MO concentration between 10 to 100 mg/L to provide us several informations about the adsorption behavior using two famous models: Langmuir and Freundlich to fit the equilibrium experimental data of MO adsorption into our activated carbon. Thermodynamic behavior was also studied by varying the temperatures (20-60°C) using 60 mg of adsorbent mixed with 1000 mL of the MO dye solution at pH=2.

3. Results and discussion

3.1 Characterization of the biosorbent:

The total surface area (or BET surface area S_{BET}) is one of the most widely known parameters associated with activated carbons [5]. The Table 1 presents the textural properties of *Ziziphus* activated carbon. The S_{BET} of this low-cost activated carbon is $553 \text{ m}^2\cdot\text{g}^{-1}$, this value is higher than $377 \text{ m}^2\cdot\text{g}^{-1}$ reported by Wang et al., (2011) [6] using activated carbon from sewage sludge. A light difference is observed using commercial activated carbon with $564 \text{ m}^2\cdot\text{g}^{-1}$ [7] However, [8] Anisuzzaman et al., (2015) found $966.74 \text{ m}^2\cdot\text{g}^{-1}$ with activated carbon from *Typha orientalis* leaves. Generally, adsorption capacities

increase in the growth of this parameter [9, 10]. While there are various exceptions to other types of activated carbon [10, 11].

Table 1: Chemical and textural properties of the activated carbon.

Properties	Value
Textural BET surface area (m ² /g)	553.39
Micropore volume (cm ³ /g)	0.156
Micropore area (m ² /g)	307.25
Mesoporous volume (cm ³ /g)	0.163
Total vol. BJH (cm ³ /g)	0.319

The SEM analysis was also performed. The Fig. 1 shows the SEM images of the activated carbon at 2400 magnifications. This result confirms those obtained using BET analysis and indicated a large development of pores that are clearly found on the surface of the *Ziziphus Lotus* activated carbon, this could be thanks to the activation process using the phosphoric acid (H₃PO₄) as chemical activating agent [12]. Also, we notice the presence of heterogeneous pores which are essential for the adsorption of different types of pollutants [13]. Thus, it can be claimed that the surface of *Ziziphus* leaves activated carbon has a nanoporous structure. Similar observations were reported by Ricou-Hoeffler et al., (2001) [14] and Hameed and Daud (2008) [15] using fly ash and agricultural waste activated carbon, respectively.

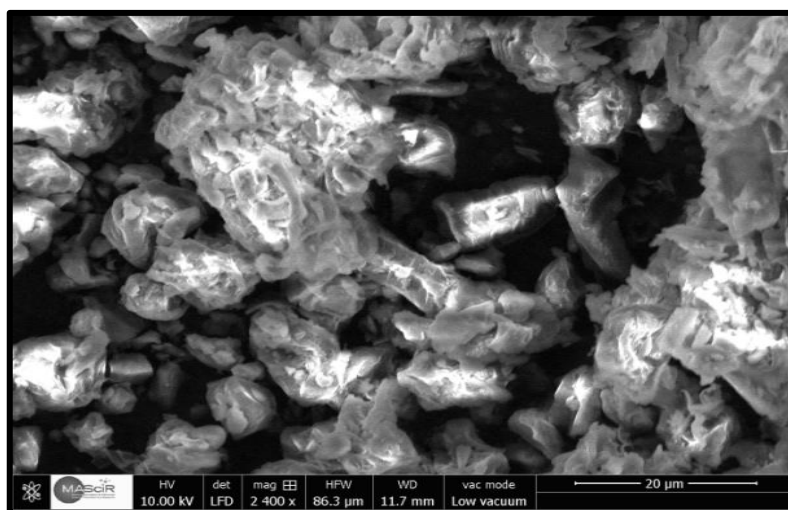


Fig.1. Scanning Electron Micrograph for the prepared activated carbon (a) × 2400.

FT-IR analysis of the bio-carbon was performed to determine the functional groups, and then evaluate the involvement of these functional groups in the adsorption of MO dye onto *Ziziphus Lotus* leaves activated carbon. The Fig.2 (a) display the spectra of the activated carbon, the band located between 3200 and 3600 cm^{-1} can be attributed to the hydroxyl groups -OH to lignin [16] and the hydrogen-bonded OH vibration of the cellulosic structure. The band observed around 1610 cm^{-1} could be attributed to the stretching of the aromatic rings ($\text{C}=\text{C}$). The band at 1223 cm^{-1} is partly associated with C-O stretching and O-H bending modes in the functional group, the band at around 1080 cm^{-1} can be attributed to the C-OH stretching of phenolic groups, also it can be seen a band around 640 cm^{-1} that justify the presence of the out-of-plane deformation mode of O-H of cellulose [17]. The presence of lignin and cellulose structure suggest a lignocellulosic structure of active and carbonized *Ziziphus Lotus*, this structure is also observed for other carbon, such as Brazilian coconut shell and Tunisian olive-waste cakes [18]. It is well acknowledged that the polyphenolic compounds like lignin groups present in lignocellulosic materials are the active sites for attachment of ions, the use of these materials in the natural state, without any treatment, can cause problems of lower durability, leaching of soluble organic components at strong acidic and basic media, and lower adsorption capacity.

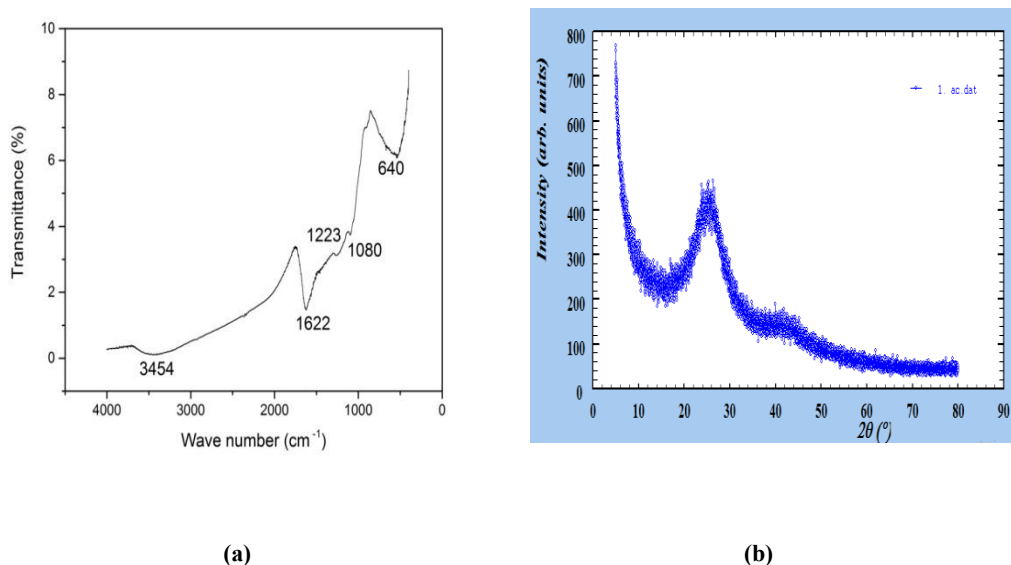


Fig.2. (a) FTIR and (b) XRD spectra of *Ziziphus lotus* activated carbon

The XRD spectrum of activated carbon was also performed in the Fig.2 (b). It indicates the presence of broad diffraction background and the absence of a sharp peak reveal a predominantly of amorphous structure [19]. The amorphous structure of the activated carbon was revealed by several products such as oil palm, empty fruit brunch and coconut shell [20].

3.2 Kinetic studies:

The first and second-order kinetic models were plotted (Fig. 3); Table 2 resumes the obtained results. The validity of each model was evaluated by the fitness of the straight line (R^2), from the results we observed that the adsorption of MO was better fitted with the pseudo-second-order with a $R^2=0.99$, The Table.2 shows the kinetic models parameters; the high equilibrium adsorption q_e (769.23mg/g) at an equilibrium time of 10min indicates a high degree of affinity existing between MO and our activated carbon.

Table 2. Adsorption kinetic parameters of Methyl Orange on *Ziziphus leaves* adsorbent

Pseudo-second order			Pseudo-first order	
Qe (mg/g)	K ₂ (g /mg .min)	R ²	K ₁ (min ⁻¹)	R ²
769.23	3.67.10 ⁻⁴	0.99	0.0175	0.90

These results indicate that the kinetic model of the adsorption is based on the assumption that the rate-limiting step is a chemical adsorption involving valance force through sharing or exchange of electrons between adsorbent and adsorbate. A similar result was also obtained by [21] Huang et al, (2013) using protonated cross-linked chitosan.

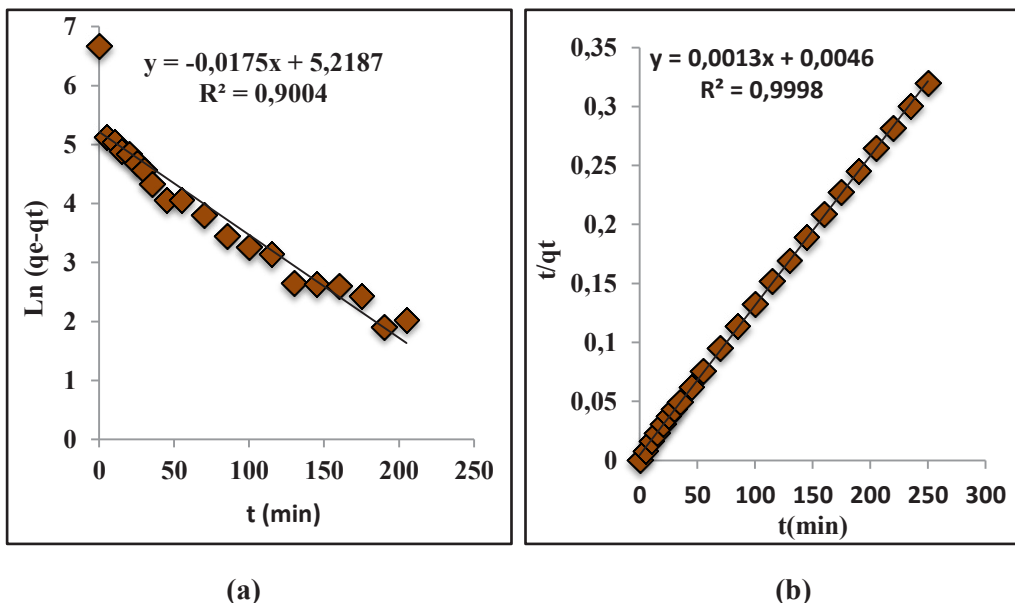


Figure.3. Adsorption kinetic models of MO on *Ziziphus* activated carbon (a) pseudo-first-order, (b) pseudo-second-order model.

3.3 Adsorption isotherm study:

Freundlich and Langmuir isotherm models explain the capacity of the adsorbent, the interaction between the solute-solution and the nature of adsorbed accumulation materials on the surface. The Fig. 4 shows the plot of Langmuir and Freundlich isotherm models. The results shown in Fig.4 revealed that the sorption of MO on *Ziziphus Lotus* adsorbent is the monolayer type since the Correlation coefficient ($R^2=0.99$) calculated from Langmuir isotherm, which indicates the applicability for the Langmuir isotherm. The results are in accordance with the literature, where Chen et al., (2011) [22] were found the same behavior of MO on the surfactant-modified silkworm exuviae.

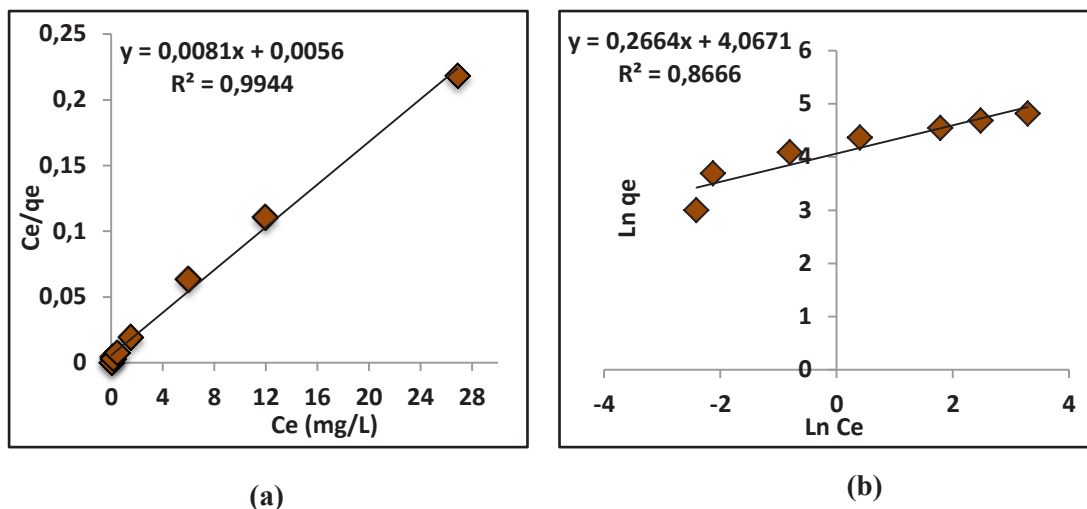


Figure.4. Adsorption isotherm of MO on *Ziziphus* activated carbon (a) Langmuir model, (b)

Freundlich model

3.4 Thermodynamic studies:

The effect of temperature (20, 40, 50 and 60 °C) on the adsorption of MO by our activated carbon was studied. The values of ΔH^0 and ΔS^0 can be calculated from the slope and the intercept of the plot of $\ln K_L$ versus $1/T$, respectively, when the values of ΔG^0 were calculated using the thermodynamic equations (Table 3), that indicates a physisorption type of the MO sorption. The negative values of overall free energy changes during the adsorption process indicate the spontaneous nature of the adsorption process. The positive value of ΔS^0 (72.74 J/mol.K) resulted from the increased randomness due to the adsorption of MO, similar thermodynamic behavior was obtained by Subbaiah and Kim, (2016) [23] using aminated pumpkin seed powder.

Table 3. Thermodynamic parameters of adsorption of MO onto *Ziziphus lotus* adsorbent

T (°K)	1/T	Ln K _d	R ²	ΔS° (J/mol.K)	ΔH° (j/mol)	ΔG° (J/mol)
333	0.0030	2.788	0.991	72.74	16489.15	-7721.15
313	0.0031	2.390				-6221.03
293	0.00347	1.930				-4703.41

Conclusion

The present work shows that a new activated carbon can be prepared from *Ziziphus* leaves through phosphoric acid activation. *Ziziphus* leaves were selected as a suitable agriculture product thanks to its abundance in Morocco and its disposal in the environment without any treatment. Several parameters were studied to deduce their effect on Methyl Orange adsorption. Adsorption of Methyl orange onto our activated carbon increases with decreasing temperature, with decreasing pH and with increasing concentration, as expected from the law of mass action, in the range studied. The results show that the pH =2, adsorbent dose of 60mg and very low contact time of 10min are sufficient to eliminate 97% of MO.

The adsorption isotherm was well fitted with the Langmuir model and show that the adsorption is the monolayer type, the adsorption rate process is best described by the Lagergren pseudo-second-order rate model.

The kinetic study shows that the adsorption follows the pseudo-second-order model and the thermodynamic study revealed that the adsorption was the type spontaneous and endothermic. Finally, we can relate the *Ziziphus* lotus activated carbon efficiency to the nature and the chemical structure of the product found by BET, SEM-EDX, FT-IR and DRX analysis.

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