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Industrial wastewater decolorization by activated carbon from *Ziziphus lotus*

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ABSTRACT

This work deals with the adsorptive treatment of textile wastewater by novel activated carbon prepared from *Ziziphus lotus* leaves. The effect of experimental parameters (pH, adsorbent dosage, dye concentration, adsorption time, and temperature) and the optimal adsorption conditions for the degradation of the wastewater were investigated. After 5 h of treatment, the results were 97.41% elimination of color and 73.96% elimination of chemical oxygen demand. The kinetic data for the adsorption process were found to fit pseudo-second-order rate equations. The Langmuir isotherm model turned out to be the most accurate one while the thermodynamic study revealed the adsorption to be endothermic and spontaneous. To explain the effectiveness of the treatment, the activated carbon was characterized by scanning electron microscopy, Brunauer–Emmett–Teller, X-ray diffraction, and Fourier-transform infrared spectroscopy.

Keywords: Textile wastewater; Adsorption; *Ziziphus lotus*; COD; Turbidity

1. Introduction

In recent years, heavy metals and textile dye effluents have become one of the most important and dangerous sources of environmental pollution, due to their high toxicity toward aquatic life, animals, plants, and humans [1]. Disposal of textile wastewater into the environment is a major source of environmental contamination; this wastewater is characterized by a significant chemical oxygen demand (COD), an intense color, a high content of suspended matter, and a very alkaline pH [2]. Moreover, the intense color of textile wastewater inhibits light penetration into receiving waters, thus hampering biological processes and photosynthesis [3]. In this context, decolorization of wastewater containing textile dyes is an absolute necessity for the preservation of water resources and the environment. Several techniques are used for treatment of textile dyes, some of which are membrane techniques, coagulation–flocculation, electrochemical processes, advanced oxidation, and adsorption processes [4]. Among these techniques, adsorption has drawn a great deal of attention because of its appealing features: it can be readily operated; it generates sludge exempt of chemicals unlike conventional wastewater treatment; and it is selective, economic, and effective [5].

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The process utilized in our study employs activated carbon (AC), a material which has found a wide array of applications in fields such as biomedicine, catalysis, separation and purification of liquids and gases, elimination of industrial pollutants, etc. [6]. AC is extensively used as adsorbent because of its high adsorption capacity to eliminate a large number of organic compounds. Nonetheless, its high production cost, difficulties associated with its regeneration, and its negative environmental effect limit its usage, and encourage scientists to seek eco-friendlier and low-cost alternatives [7]. Recently, various studies have suggested utilizing organic and natural materials as low-cost adsorbents. Existing literature reports have identified numerous low-cost bio-products such as cactus (*Opuntiaficus indica*) [8], agricultural wastes [9], and AC using the waste of cassava (*Manihot esculenta* Crantz) for wastewater treatment [10]. Our work is focused on the feasibility of AC from a new source: jujube *(Ziziphus lotus),* a shrub species common in arid and semi-arid regions including those of Morocco. Interestingly, constituents of this abundant plant remain unexploited, hence the idea of turning its leaves into a value-added product: AC. The study reported herein proposes the valorization of these leaves as an inexpensive and eco-friendly material to be used in the treatment of textile wastewater collected from a Moroccan jeans factory.

Previously reported work on the use of *Z. lotus* in the field of wastewater treatment is very limited. One such work, reported by El Messaoudi et al. in 2017 [11] deals with the use of jujube shells of *Z. lotus* as a sorbent to remove Congo red from aqueous solutions. The authors obtained an adsorption capacity of 59.55 mg/g. To the best of our knowledge based on an extensive review of the existing literature, the study reported herein is unique in the sense that our *Z. lotus* leaves-based biomaterial has never been used previously.

In this work, *Z. lotus* leaves were chemically activated with phosphoric acid and carbonized. Characterization by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), and X-ray diffraction (XRD) was performed. Determination of the point of zero charge of pH (pH_{ZPC}), moisture content, ash, volatile matter, and methylene blue number (MBN) were done as well.

Assessment of the performance of our AC in the treatment of textile wastewater was carried out by varying several parameters, namely pH, temperature, mass of adsorbent, contact time, and dye concentration. Finally, an adsorption mechanism of *Ziziphus* leaves-derived carbon is proposed through adsorption isotherms, kinetics, and thermodynamics.

2. Materials and methods

2.1. Textile wastewater and reagents

Textile wastewater used in this work was obtained from a jeans factory located in the region of Casablanca-Settat, Morocco; effluent samples were taken at various stages of the manufacturing process. The wastewater physicochemical characteristics such as pH, conductivity, turbidity, COD, and biochemical oxygen demand (BOD) were performed before and after adsorption.

2.2. Adsorbent preparation and characterization

Z. lotus leaves were also obtained from the Casablanca-Settat region, Morocco. These leaves were washed several times with distilled water to remove residues and oven-dried at 75°C for 24 h, after which they were ground. The *Z. lotus* AC was synthesized using the raw ground material. To determine the optimal production conditions of the sorbent, three factors influencing the synthesis were selected: impregnation ratio material:H_3PO_4 (1–3), carbonization temperature (200°C–800°C), and time of carbonization (30–120 min). The yield of methylene blue elimination was the parameter chosen as a "response", in order to optimize the AC synthesis conditions using Box–Behnken model. Optimal conditions of production of our AC were found to be an H_3PO_4 impregnation ratio of 2.76, carbonization temperature of 413°C, and carbonization time of 72 min. Finally, the AC was neutralized, dried at 60°C for 6 h and sieved to sizes between 40 and 63 μm.

pH_{ZPC} was measured by mixing 50 mL of 0.1M KNO_3 solution with 0.1 g of our AC to form a suspension which was stirred for 48 h at room temperature (25°C ± 1°C). Moisture content, volatile matter, MBN, and ash content of the adsorbent were analyzed according to American Society for Testing and Materials standards. Physicochemical properties of the material were also determined. Specific surface area (S_{BET}) was determined by BET method with a Micromeritics machine model 3 Flex 3500, the surface morphology and the elemental composition were acquired by SEM and energy-dispersive X-ray using a FEI Quanta 450 FEG Environmental Scanning Electron Microscope. FTIR spectroscopy was performed by a SHIMADZU FTIR-8400S, and XRD measurement was done using a D2 PHASER-BREKUR.

2.3. Adsorption experiment

Adsorption experiments were carried out to determine the effect of parameters influencing the textile dye elimination by our adsorbent. A UV-visible spectrophotometer (Hach Lange DR 6000) was used to determine the λ_{max} of the dye present in the industrial wastewater. λ_{max} in the visible light region was found to be 610 nm (Fig. 1), which matches the λ_{max} of indigo carmine. An initial indigo carmine concentration in industrial wastewater of 252.17 mg/L could be determined by means of a calibration curve. After treatment, the mixtures were centrifuged at 7,500 rpm for 5 min with a centrifuge (Sigma Laborzentrifugen 2-15), and

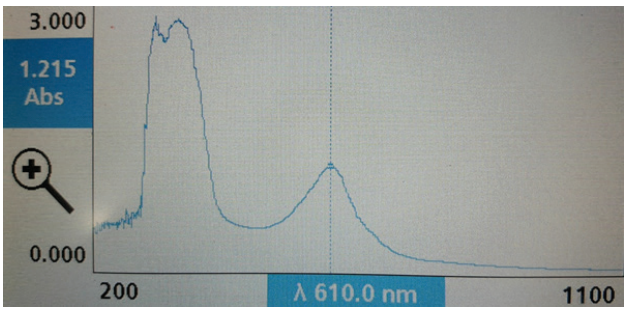

Fig. 1. UV-Vis absorption spectrum of industrial wastewater with maximum absorption at 610 nm.

the supernatant absorbance was determined. The amount of adsorbed dye per gram of AC and the removal percentage at equilibrium, denoted by q_e (mg/g) and Y (%), respectively, were calculated using Eqs. (1) and (2):

$$q_e = \frac{(C_0 - C_t)V}{W} \tag{1}$$

$$Y(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

where C_0 (mg/L) is initial concentration of indigo solution; C_t (mg/L) is concentration of indigo at time t; V (L) is volume of the solution; and $W(g)$ (g) is weight of dry adsorbent used.

2.3.1. Optimization of pH and adsorbent dosage

A textile solution of 50 mL with an initial concentration of 252.17 mg/L was placed into several 250 mL beakers. The optimal pH value was determined by varying the initial pH of the dye solution to the desired value from 2 to 12; pH adjustment was done using either 0.1N NaOH or 0.1N HCl, with an adsorbent dosage ranging from 0.02 to 1 g/L. Solutions were agitated in a BOD meter (WTW OxiTop IS 12) at a constant speed and ambient temperature for 24 h.

2.3.2. Adsorption kinetics

The pseudo-first-order and pseudo-second-order models were applied in this work to determine the adsorption kinetics characteristics. To this end, the kinetics of the adsorption process was monitored under the following conditions: a fixed amount of adsorbent of 0.6 g/L, an initial dye concentration of 252.17 mg/L, and an agitation time in the range of 2–600 min.

The pseudo-first-order model suggests that the adsorption is reversible and that the adsorption rate at time t is proportional to the difference between the amounts adsorbed at equilibrium, q_e, and at time t, q_t [12]. This model is expressed by Eq. (3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where k_1 (g/mg min) is rate constant of the pseudo-first-order kinetic model.

The linear relationship between $\ln(q_e - q_t)$ and t was used to compute the theoretical equilibrium adsorption concentration q_e, and the rate constant k_1. Values of q_e and k_1 were calculated from the slope and intercept.

The pseudo-second-order kinetic model was established using Eq. (4) to have a suitable prediction of the adsorption kinetics process of the textile dye using our AC [12]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{4}$$

where q_t (mg/g) is amount of dye adsorbed at time t; q_e (mg/g) is amount of dye adsorbed at equilibrium; and k_2 (g/mg min) is rate constant of the pseudo-second-order kinetic model.

Pseudo-second order was determined by plotting t/q_t as a function of t, thus enabling the calculation of q_e and k_2 from the slope and intercept.

2.3.3. Isotherm studies

50 mL of textile dye solutions at concentrations ranging from 252.17 to 25.21 mg/L was prepared by dilution with distilled water. Each solution was then mixed with 50 mg of AC at a fixed time, pH, and temperature in order to fit and interpret the experimental results of Langmuir and Freundlich isotherm models.

On the one hand, the Langmuir isotherm assumes that adsorption occurs at a specific number of homogeneous sites, with formation of monolayers. The linear form of the Langmuir isotherm [13] is given in Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{5}$$

where q_e (mg/g) is equilibrium dye concentration on the adsorbent; C_e (mg/L) is equilibrium dye concentration in the solution; $q_{\max}$ (mg/g) is maximum adsorption capacity of the adsorbent; and K_L (L/mg) is Langmuir adsorption constant.

On the other hand, the Freundlich isotherm is an empirical model used to describe the adsorption characteristics for the heterogeneous surface; the Freundlich isotherm equation is given in Eq. (6) [14]:

$$\log q_e = \log K_F + \left(\frac{1}{n_F}\right) \log C_e \tag{6}$$

where q_e (mg/g) is equilibrium dye concentration on the adsorbent; C_e (mg/L) is equilibrium dye concentration in the solution; K_F [(mg/g) (L/mg)$^{1/n}$] is proportionality constant; and $1/n_F$ is adsorption intensity.

2.3.4. Thermodynamic studies

To study the effect of temperature, adsorption studies of the textile effluent onto the *Z. lotus* adsorbent were performed at different temperatures (25°C–60°C), using 50 mg of adsorbent mixed with 50 mL of textile dye solution. Initial pH and concentration were 10.32 and 252.17 mg/L, respectively. Finally, samples were shaken for an optimal period of time. Calculation of change in Gibbs free energy $\Delta G°$, change in enthalpy of adsorption $\Delta H°$, and change in entropy $\Delta S°$ gave insight about the thermodynamic behavior of adsorption. These thermodynamic functions and equilibrium constant K_d for this adsorption process were determined by using Eqs. (7)–(9) [15]:

$$K_d = \frac{q_e}{C_e} \tag{7}$$

$$\Delta G° = -RT \ln K_d \tag{8}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where K_d (L/mg) is equilibrium constant for this adsorption process; q_e (mg/g) is equilibrium dye concentration on the adsorbent; C_e (mg/L) is equilibrium dye concentration in the solution; R (J/mol K) is universal gas constant, 8.314; and T (K) is absolute temperature of the solution.

Values of K_d and ΔG° could be calculated directly at different temperatures based on Eqs. (7) and (8). ΔH° and ΔS° were calculated from the slope and intercept of the plot $\ln K_d$ vs. $1/T$.

3. Results and discussion

3.1. Characterization of the AC

Physicochemical and adsorptive characteristics of our adsorbent were determined prior to its use in the adsorption process—data are shown in Table 1. Our biosorbent was found to have a pH_{ZPC} of 7.7, and a moisture content (7.2%) higher than the ash content (0.61%). In the carbonization and activation processes, volatile matter is released as gas and liquid products which evaporate off thus producing ultimately a material with high carbon content. The volatile matter content of our adsorbent (0.69%) turns out to be much lower than the 21.31% and 17.50% obtained by acid activated *Moringa oleifera* carbon and commercial AC by Bello et al. [16]. This indicates a carbon skeleton, and a rudimentary pore structure is formed. The small particle size of our AC (<63 μm) has a positive effect on the adsorption process. Indeed, Saeidi and Lotfollahi [17] reported that a decrease in AC particle size from 150 to 50 μm results in a substantial increase of both iodine number and surface area. Another important measurement is the MBN; it is used to analyze the presence of microporosity (>1.5 nm) and mesoporosity and is a good indicator of the adsorption of large molecules. Table 1 shows an MBN value of 833.3 mg/g achieved using our AC; higher than the 150 mg/g obtained with industrial AC Darco G-60 (Sigma-Aldrich, USA), and the 380 mg/g reported by Jadhav and Mohanraj [18] using AC from *Cocos nucifera* leaves (coconut leaves generated as agricultural waste). An MBN greater than 400 mg/g indicates that carbon is good for dye adsorption; presumably, this high value is attributed to the widening of some micropores caused by the liberation of volatile matter at high temperature. Table 2 presents the textural properties of our *Ziziphus* adsorbent.

Table 1
Physical properties of *Ziziphus* biosorbent

Parameter	Data
pH_{ZPC}	7.7
Moisture content (%)	7.20
Ash content (%)	0.61
Volatile matter (%)	0.69
Particle size (μm)	<63
MBN[a] (mg/g)	833.33

[a]Methylene Blue Number (MBN).

The surface area, S_{BET}, is a key characteristic of AC. The S_{BET} of this low-cost adsorbent is 553 m^2/g; comparatively, this is slightly smaller than commercial AC (564 m^2/g [19]), but much smaller than the one prepared from prickly pear peel (1,433 m^2/g [20]) and sugarcane bagasse (1,025 m^2/g [21]). Generally, adsorption capacity increases with the growth of this parameter [20], though there are exceptions as illustrated by the work of Pelaez-Cid et al. [20] and Valix et al. [21]. In their studies, adsorption capacities of methylene blue were measured to be 416.7 and 384.6 mg/g, respectively, whereas our material is characterized by an MBN of 833.33 mg/g (Table 1) and a lower surface area. Consequently, one may suggest that the surface area of a given sample of AC is not necessarily proportional to its adsorption capacity. Reportedly, a high adsorption capacity is obtained when the carbon has a large number of pores, the size of which is slightly larger than the size of the molecule to be adsorbed [22]. For the adsorption of high molecular weight materials such as colored compounds or humic substances, carbon with a high mesoporosity is required, but a high total surface area is not essential [23]. According to Pelaez-Cid et al. [20], the volume of mesopores (V_{MesoP}) can be calculated using the difference between total pore volume (V_{TP}) and the micropore volume (V_{micP}). As shown in Table 2, volumes of 0.156 and 0.163 m^3/g for micropores and mesopores, respectively, have been measured in our material; these two parameters are crucial in the adsorption process because they facilitate the access to the micro and macromolecules into the carbon particles. Saeidi et al. [24] stated in their study that increase of the surface area, the mesoporous structure, and the pore volume all play a major role in the adsorption process when applied to wastewater treatment. As mentioned previously, *Z. lotus* AC has an average surface area of 553 m^2/g and a high mesoporous structure, so it has enormous potential in the treatment of industrial wastewater (textile dye wastes in the present case).

In order to further characterize our product, SEM analysis was performed. Fig. 2 shows SEM images of the adsorbent at 2,400 and 4,000 magnifications. Micrographs confirm results obtained using BET analysis and indicate a large development of pores which is clearly found on the surface of the *Z. lotus* AC. This could result from the activation process using phosphoric acid, H_3PO_4, as a chemical activating agent. Also, we notice in Fig. 2(b), the presence of heterogeneous pores which provide grounds that the surface of *Ziziphus* leaves AC has a porous structure; this is in line with observations reported by Hameed and Daud [25] using agricultural waste AC. Energy dispersive X-ray spectroscopy (EDX) spectra of the biosorbent consist of C (83.98%)

Table 2
Chemical and textural properties of the biosorbent

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 volume (Barrett, Joyner, Halenda method of determination of pore size distribution) (cm^3/g)	0.319

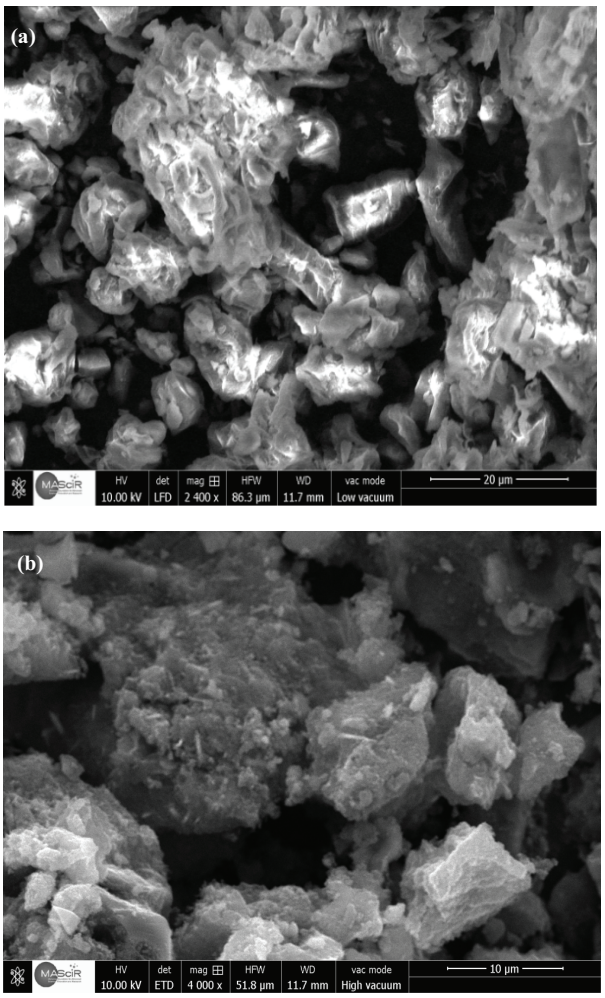

Fig. 2. Scanning electron micrographs of synthesized activated carbon (a) ×2,400 and (b) ×4,000.

and O (14.17%) as the major constituents of the product and the presence of other minor elements such as P (0.93%), Na (0.66%), Ca (0.14%), and Si (0.12%) in the structure (Fig. 3). The presence of phosphorus and sodium may be due to the H_3PO_4 and NaOH used in the activation and neutralization steps required to prepare AC. As for the presence of Si and Ca, they most likely come from the *Z. lotus* leaves, because the concentration of these elements in the leaf and the AC are nearly identical (Figs. 3(a) and (b)). Concerning carbon, the high content of this element indicates a high degree of graphitization as well as low contents of functional groups; on the other hand, the oxygen content suggests the presence of acid functional groups [26]. Comparatively, Van and Thi [27] obtained similar levels of C and O (83.04% and 16.96%) to ours, in their work with rice husk-derived AC.

Adsorption efficacy is not only related to the surface areas, but also depends on the chemical properties on the surface of the adsorbent. FTIR analysis of our bio-carbon was performed to determine the functional groups, and then evaluate their involvement in the adsorption of textile dye onto *Z. lotus* derived AC. Spectrum of the adsorbent is shown in Fig. 4. The band located between 3,200 and 3,600 cm^{-1} can be assigned to the hydroxyl groups –OH of lignin and the hydrogen-bonded OH

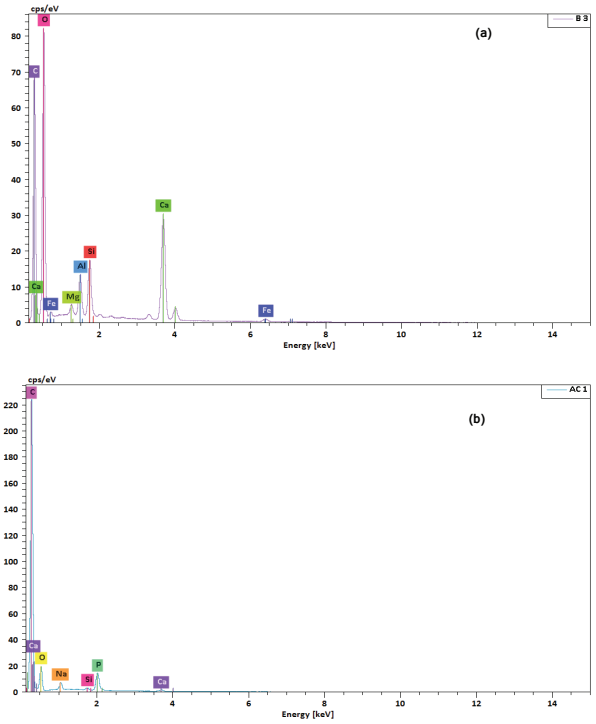

Fig. 3. EDX spectra of *Ziziphus* leaves: (a) raw material and (b) activated carbon.

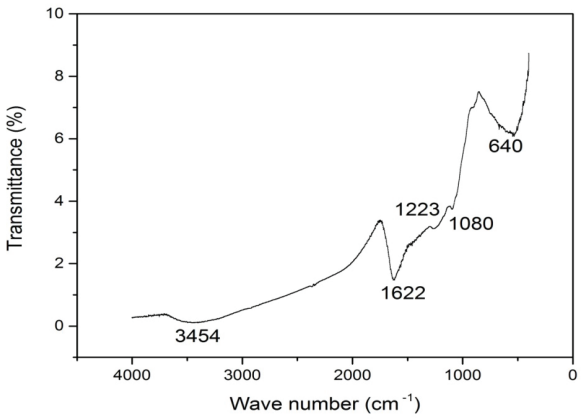

Fig. 4. FTIR spectrum of activated carbon from *Ziziphus lotus*.

vibration of the cellulosic structure [28]. The bands observed at around 1,610 cm^{-1} could be attributed to the stretching of the aromatic rings (C=C) [29]. The band at 1,223 cm^{-1} is partly associated with C–O stretching and O–H bending modes in the functional group [30]; the band at around 1,080 cm^{-1} can be attributed to the C–OH stretching of phenolic groups [31]. Finally, a band at around 640 cm^{-1} justifies the presence of the out-of-plane deformation mode of O–H of cellulose [32]. The presence of both lignin and cellulose suggests a lignocellulosic structure of activated and carbonized *Z. lotus*; this structure is also observed in other carbon materials, for example, olive-waste cakes [33]. It is known that the active sites for attachment of ions are the polyphenolic compounds such as the lignin groups present in lignocellulosics [34].

The XRD spectrum of AC was also obtained (Fig. 5). The spectrum shows predominantly an amorphous structure, which is an advantageous property for adsorbents. However, the occurrence of broad peaks around 26° and 43°, corresponding to plans (002) and (100), respectively, is attributed to the reflection of graphite [35]. Based on the literature [35], these peaks provide evidence that our AC consists of small sp^2 platelets. AC from various sources is mostly amorphous as corroborated by XRD patterns of several products available in the literature (palm oil, empty fruit brunch, coconut shell, etc.) [36].

3.2. Physicochemical characteristics of the textile effluent

In the textile industry, various chemicals such as sulfur, naphthol, nitrates, acetic acid, dyes, and certain auxiliary chemicals are used. Textile dye effluents samples used in this study were typically dark blue in color and malodorous. Table 3 summarizes the physicochemical parameters of one textile dye effluent sample and compares them with standards. Before treatment, the effluent has a very basic pH (10.3), a high dye concentration (252.17 mg/L), and high values of BOD and COD (890 and 2,880 mg/L). It is noteworthy that the COD/BOD ratio is here higher than 3, thus highlighting the difficulty for this effluent to biodegrade. Last but not least, the physicochemical parameters of our sample exceed by far those fixed by the World Health Organization and by the Moroccan Directorate of Water Research and Planning. In this regard, Khlifi et al. [37] reported similar values for textile effluents in Poland. With pollutants being overly concentrated, depollution of these effluents is of paramount importance to enable the textile dye industry to comply with environmental regulations.

3.3. Effect of pH on textile wastewater adsorption

Solution pH is an important parameter influencing the adsorption process and principally the adsorption capacity. The plots of percentage removal of color, COD, and turbidity vs. pH are shown in Fig. 6. There is an increase of removal yield for the three parameters, especially the color as pH increases from 2 to 10. However, at pH 12 all the three parameters decrease. When pH_{pzc} > pH (i.e., AC surface is positive), there is a significant increase of decolorization, and when pH_{pzc} < pH (i.e., AC surface is negative) the decolorization increases slightly due to the attractive electrostatic forces [38]. The pKa value of the indigo carmine dye present in the industrial wastewater is 12.2. When the pH is in the range of 2–10, where the dye is in its acidic form, the decolorization increases with increase in pH. However, at pH 12 and above, the increase of pH caused a reduction in the decolorization. Souza et al. [39] suggested that this increase of adsorption can be attributed to the solubilization of organic groups present on the surface of the adsorbent. Yet, Ramesh and Sreenivasa [40] believe this behavior is caused by the presence of negatively charged hydroxyl ions in the solution, in addition to the surface of our AC. Based on these

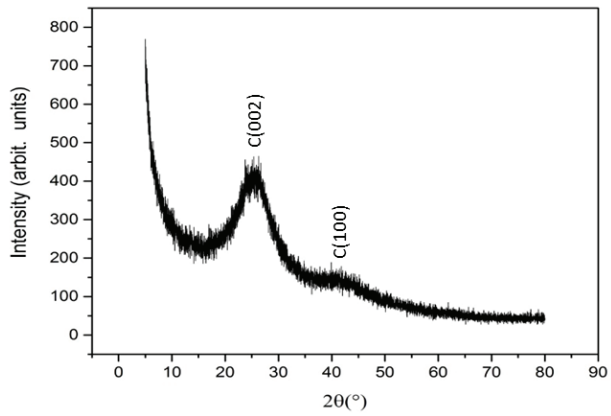

Fig. 5. XRD spectrum of activated carbon from *Ziziphus lotus*.

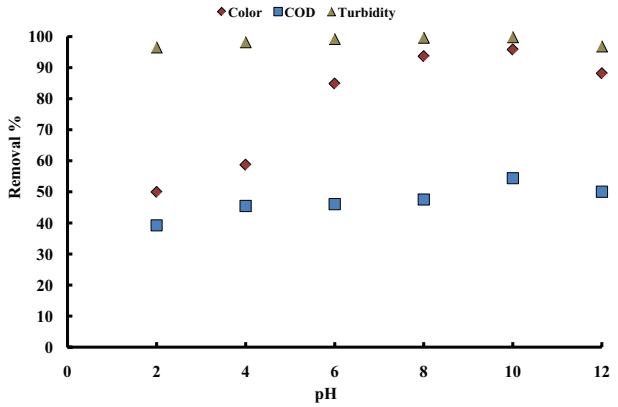

Fig. 6. Effect of pH on textile wastewater treatment.

Table 3
Textile effluent standards and physicochemical characteristics before and after treatment

Parameter	Moroccan Standard	World Health Organization Standard	Value of textile effluent	
			Before treatment	After treatment
pH	6–9	6.5–8.5	10.32	9.30
Dye concentration (mg/L)	–	–	252.17	6.52
Suspension matter (mg/L)	50	<20	8,030	–
Turbidity (NTU)	–	–	350	0.46
BOD (mg O_2/L)	140	<30	890	–
COD (mg O_2/L)	500	<90	2,880	750
Color	Colorless	Colorless	Blue	Colorless

results, we can conclude that the optimal pH of adsorption of the textile wastewater is between 7 and 10. The pH of our raw effluent being about 10.32, no pH adjustment is therefore required.

3.4. Effect of adsorbent dosage on textile wastewater adsorption

The adsorption process is also affected by another critical factor: the adsorbent dosage. The effect of this factor was tested experimentally by varying the quantity of AC between 0.02 and 1 g/L at optimal pH. Results are shown in Fig. 7. As expected, an increase of the dosage caused both color and turbidity removal in the wastewater; up to 97.4 % for color removal and up to 93.8 % for turbidity removal. Regarding COD, increasing the dosage resulted in a COD reduction ranging from 40% to 74%. The optimal *Z. lotus* AC dosage was determined to be 0.7 g/L, based on the fact that no significant evolution of the COD, color, and turbidity is detectable above this value. Ahmad and Hameed [41] reported that, in their case, the maximum removal of color and COD from textile dye wastewater was 89.13% and 72.11%, respectively, by using a higher dose of 3 g/L of bamboo-based AC.

3.5. Effect of contact time on textile wastewater adsorption

To appraise the effect of contact time on textile wastewater adsorption, a graph of wastewater adsorption capacity as a function of contact time was plotted (Fig. 8). The latter demonstrates that the adsorption capacity q_e of the indigo dye increases with contact time. Indigo adsorption progresses over time from 200 to 315 mg/g, achieved in 5 and 300 min, respectively. After 300 min, there is no significant increase of adsorption capacity with the increase in time, due to the saturation of the active sites in our AC.

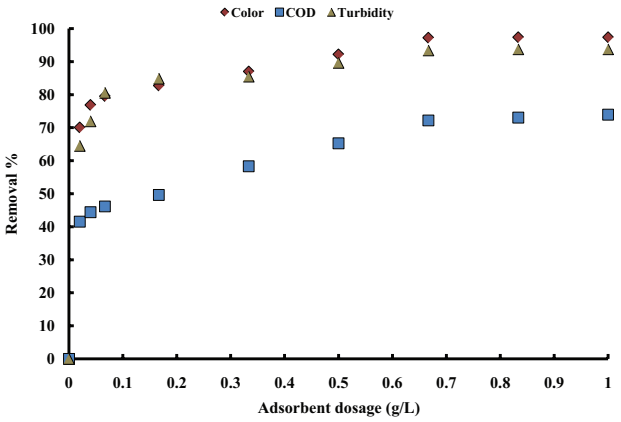

Fig. 7. Effect of adsorbent dosage on textile dye treatment.

3.6. Adsorption kinetics

The kinetic study of adsorption processes provides useful information about the sorption efficiency and feasibility [41]. Three kinetic models were applied to study the kinetics of adsorption: pseudo-first order, pseudo-second order, and intraparticle diffusion. Table 4 summarizes the results obtained from these three models. Data obtained were found to conform best to a pseudo-second-order model with a coefficient of determination, R^2 of 0.99. Next, to a pseudo-first-order model (R^2 = 0.90), while, the intraparticle diffusion model gives the lowest coefficient of determination (R^2 = 0.73). Moreover, the pseudo-second-order adsorption capacity at equilibrium is the closest to the experimental one. Consequently, the pseudo-second-order model appears as the most accurate model to interpret our experimental data. Oguntimein [42] also reported that the pseudo-second-order model is the most appropriate one to represent adsorption kinetics of textile dye onto sunflower seed hull-derived carbon.

3.7. Adsorption equilibrium and isotherm models

The isotherm parameters of Langmuir and Freundlich models are presented in Table 5. The validity of each model was tested by comparing the coefficient of determination.

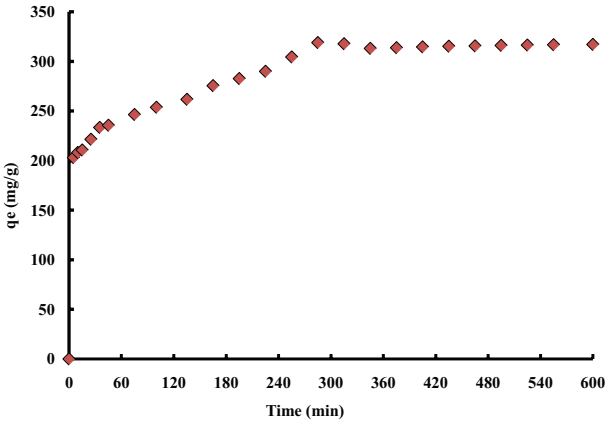

Fig. 8. Effect of contact time on textile dye treatment.

Table 5
Characteristic parameters obtained by the Freundlich and Langmuir equations

Langmuir isotherm			Freundlich isotherm		
K_L (L/mg)	Q_{max} (mg/g)	R^2	$1/n_F$	K_F (L/g)	R^2
1.50	3,333.33	0.99	0.05	22.56	0.91

Table 4
Adsorption kinetic parameters of textile water onto *Ziziphus* leaves adsorbent

Pseudo first order			Pseudo second order			Intraparticle diffusion		
q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2	K_{id} (mg g^{-1} min$^{-0.5}$)	C (mg/g)	R^2
172.43	0.010	0.98	322.58	0.0002	0.99	7.62	162.58	0.70

Langmuir isotherm gives a better fit (R^2 = 0.99) compared with the Freundlich model (R^2 = 0.91); this implies that the adsorption comes from a monolayer coverage of adsorbate over a homogenous adsorbent surface. This surface would contain a finite number of adsorption sites with no transmigration of the adsorbate in the plane of the surface [43]. The maximum Langmuir monolayer adsorption capacity was 3,333.33 mg/g. The crucial characteristics and the feasibility of the Langmuir isotherm are expressed in terms of a dimensionless constant separation factor or the equilibrium parameter (R_L) which can be defined as (Eq. (10)):

$$R_L = \frac{1}{1 + C_0 K_L} \tag{10}$$

where C_0 (mg/L) is initial textile dye concentration; and K_L (L/mg) is Langmuir adsorption constant.

The value of R_L obtained is 0.002; according to El Messaoudi [11], the biosorption of our textile dye onto *Z. lotus* AC is favorable at different concentrations ($0 < R_L < 1$). A similar behavior of the monolayer coverage was obtained by Oguntimein [42] in treatment of textile dye using AC from sunflower seed hull; however, his study exhibited a very low adsorption capacity of 169 mg/g compared with our sorbent capacity of 3,333.33 mg/g.

3.8. Biosorption thermodynamics

Determination of thermodynamic parameters was performed to get an understanding about the thermodynamic behavior of textile dye biosorption onto AC. The parameters studied were change in Gibbs free energy ($\Delta G°$—Eq. (7)), standard enthalpy ($\Delta H°$—Eq. (8)), and standard entropy ($\Delta S°$—Eq. (9)). Experimental results obtained are summarized in Table 6. $\Delta H°$ gives information about the forces involved in the sorption phenomenon. Karagozoglu et al. [44] found that the energy associated with different physical forces is 4–10 kJ/mol for Van der Waals, 5 kJ/mol for hydrophobic bonds, 2–40 kJ/mol for hydrogen bonds, 40 kJ/mol for coordination exchange, 2–29 kJ/mol for dipole bonds, and more than 60 kJ/mol for other chemical forces. In this study, $\Delta H°$ was found to be 34.20 kJ/mol, which indicates that physical forces are involved between adsorbate and adsorbent. The positive value of $\Delta H°$ and the negative values of $\Delta G°$ (Table 6) show that the adsorption process is endothermic, feasible, and spontaneous. The positive value of $\Delta S°$ suggests an increased randomness at the solid solution of the textile wastewater adsorption onto the *Ziziphus* biosorbent [45]. Similar thermodynamic results for indigo removal using adsorption in conjunction with an electrochemical process were reported by Kesraou et al. [46]. Oguntimein [42] found that dried sunflower seed hull-derived AC has a different thermodynamic behavior (positive value of $\Delta G°$ and $\Delta H°$, and negative value of $\Delta S°$).

4. Investigation of the adsorbent reusability

If AC can be regenerated after usage, it allows for more economic usage of the material and adsorption process. In this respect, the regeneration properties of our adsorbent were studied through adsorption–desorption cycles. The adsorption step was performed by mixing 30 mL of wastewater with an initial concentration of 252 mg L^{-1} with 2 mg of AC for 6 h; as for the desorption step, it was carried out by washing the adsorbed materials with distilled water and then dried at 75°C for 12 h. The results obtained for four cycles are presented in Fig. 9. As it can be seen, the sorption efficiency of our *Z. lotus* AC decreases to a very small extent over multiple cycles, thus demonstrating the fairly good reusability of our AC.

Table 6
Thermodynamic parameters of textile dye adsorption on *Ziziphus* biosorbent

Temperature (K)	R^2	Thermodynamic parameters		
		$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
298.15	0.99	–7.055	34.20	138.43
303.15		–7.793		
313.15		–9.235		
323.15		–10.352		
333.15		–12.016		

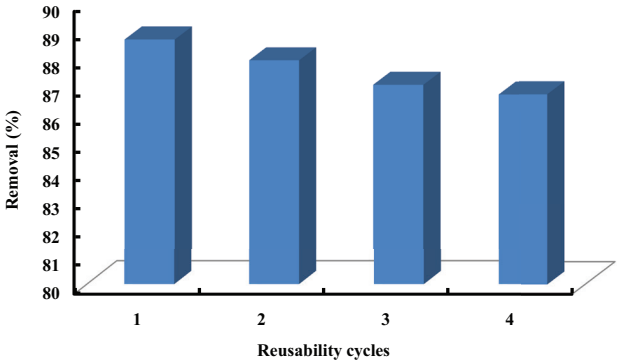

Fig. 9. Adsorption ability of the *Ziziphus lotus* activated carbon toward industrial wastewater at different cycles.

5. Conclusion

The reduction of COD and color in textile wastewater by *Z. lotus* leaves-based AC were efficient, by 73.96% and 97.41%, respectively. Characterization was done by FTIR, BET, SEM, and XRD. The pseudo-second-order model was found to be the most accurate one. Langmuir isotherm model describes well the sorption mechanism with the maximum monolayer capacity of 3,333.33 mg/g. Determination of thermodynamic parameters, $\Delta G°$, $\Delta S°$, and $\Delta H°$ shows a positive value of $\Delta H°$ and negative values of $\Delta G°$ and $\Delta S°$ indicating that the adsorption process is spontaneous and endothermic. It can be deduced from these results that the use of *Z. lotus* leaves as a source of AC is definitely an alternative low-cost and eco-friendly solution to treat industrial textile wastewater.

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