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Highly removal of anionic dye from aqueous medium using a promising biochar derived from date palm petioles: Characterization, adsorption properties and reuse studies



Amina Aichour^{a,b,*}, Hassina Zaghouane-Boudiaf^b, Hakim Djafer Khodja^a

^a Institute of Technology, University of Akli Mohand Oulhadj, Bouira, 10000, Algeria

^b Laboratory of Chemical Process Engineering, Department of Process Engineering, Faculty of Sciences and Technology, University of Ferhat Abbas Setif -1-, Setif, 19000, Algeria

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KEYWORDS

Date palm petioles; Biochar; Dyes wastewater; Methyl orange; Adsorption; Reusability **Abstract** The present work investigates the preparation of promising biochar derived from date palm petioles powder (DPB) via a thermal treatment. DPB was characterized through various techniques to analyze the chemical (FTIR), morphological (SEM) and point of zero charges to investigate changes incorporated through the pyrolysis process.

The adsorption of methyl orange (MO) onto the biochar was investigated using batch experiments according to different parameters which influence the adsorption process such as: initial dye concentration, equilibrium time, pH, and temperature. Isothermal and reuse studies of MO adsorption onto DPB were also investigated.

Results of MO removal on DPB have demonstrated that the adsorption process was initial dye concentration-dependent, and equilibrium time was occurred in 60 min. The biochar presented high stability of MO adsorption capacity in a large domain of pH. Thermodynamic analysis of this process revealed that methyl orange adsorption was exothermic and spontaneous in nature.

The experimental data were analyzed by pseudo-first-order, pseudo-second-order model, and the intraparticle-diffusion for kinetics and Langmuir, Freundlich, and Temkin models for isotherms.

Kinetic adsorption followed the pseudo-second-order model and the intraparticle-diffusion within pores controlled the adsorption rate. The experimental data yielded good fits with in the following isotherms order: Langmuir > Temkin > Freundlich, The maximum adsorption capacity of

* Corresponding author at: Institute of Technology, University of Akli Mohand Oulhadj, Bouira, 10000, Algeria.

E-mail addresses: aichouramina2@gmail.com, a.aichour@univ-bouira.dz (A. Aichour), boudiafhassina2000@yahoo.fr (H. Zaghouane-Boudiaf), h.djaferkhodja@univ-bouira.dz (H. Djafer Khodja).

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1878-5352 © 2021 Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). MO on DPB was found 461 mg.g⁻¹. The reusability study reveals the possibility of the reuse of DPB for three (03) cycles of adsorption–desorption, a slight decrease in the ability of methyl orange adsorption has noticed with the increase of the number of adsorption–desorption cycles : 81.03 %, 67.84 %, and 51.72 %, respectively. The found results of the present study show that the biochar derived from date palm petioles have the potential to be used as a promising adsorbent for the treatment of MO dye.

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1. Introduction

Nowadays, the use of dyes is increasing alarmingly, up to 10,000 dyes are available and their annual production is above 7×10^5 metric tons, which is being used not only in textile sector but also applied in paper, food and pharmaceutical industries (Bhatia et al., 2017). In some textile dyeing operations, as much as 15-20 % of dyes used do not attach to the fibers, so they are lost in wastewater, and the resulting colored effluents can represent a serious water pollution problem due to their color content and toxic components (Duran-Jimenez et al., 2014). Once dyes are dissolved in water, it is difficult to treat them, because they have a synthetic origin and a complex molecular structure, and they can persist in the environment for relatively long period of time (Forgacs et al., 2004; Vilar et al., 2011). They can therefore constitute risk factors for our health and harmful effects for our environment. It is necessary to limit these pollutants as much as possible by setting up suitable treatment means.

MO dye corresponds to the 40-sulfonic acid derivative (pKa = 3.46) (Trabelsi et al., 2013). This dye was selected as a model on the basis of its industrial consumption, water solubility, and toxicity.

There are several physical, chemical and biological methods to treat and decolorize polluted effluents such as coagulation and flocculation (Nordin et al., 2019; Huang et al., 2019), photocatalysis (Jorfi et al., 2018; Zulmajdi et al., 2020; Li et al., 2020), membrane filtration (Zinadini et al., 2014; Liang et al., 2016), chemical oxidation (Tantak and Chaudhari, 2006; Kasiri et al., 2008), ozonation (Shu and Huang, 1995; Punzi et al., 2015), ion exchange (Raghu and Basha, 2007), and adsorption (Khan et al., 2017; Lim et al., 2018; Oh et al., 2019, Suzaimi et al., 2020; Kang et al., 2020; Zhao et al., 2020; Xu et al., 2020; Kang et al., 2020). The advantages and the disadvantages of these processes are summarized in Table 1 (Crini and Lichtfouse, 2019).

Adsorption has shown a great attention for the removal of different kinds of pollutants. It is a one of the most important separation technologies today and the most favorable method for removing dyes. It has become an analytical method of choice, very efficient and simple in its use (Ahmed and Dhedan, 2012).

In the literature, there are several solid materials studied such as clays (Belhouchat et al., 2017; Oussalah et al., 2019; Aichour and Zaghouane-Boudiaf, 2020), zeolites (Ahmadi et al., 2020; Alakhras et al., 2020), activated carbon (Belayachi et al., 2019; Boudechiche et al., 2019; Ghaedi et al., 2019). Alongside these adsorbents, new ones with better properties have been developed in recent years which are the adsorbents derived from biomass. They have been recently shown a great results for the elimination of dyes from wastewater (Ani et al., 2020; Bhatti et al., 2020; Du et al., 2020; Hassan et al., 2020; Lima et al., 2021; Yeow et al., 2021).

The objective of our study is to prepare a biochar from a date palm petioles in order to obtain a new product applicable for environmental purposes, in particular for the elimination of anionic dyes that used in the textile industry. Date palm petioles were purified and calcined at 450 °C. Adsorbent properties of the obtained material were tested in removal of MO dye from aqueous medium.

2. Materials and methods

2.1. Materials

Date palm petioles (DPP) were collected from the region of Biskra in the south east of Algeria. Methyl orange (chemical formula: $(C_{14}H_{14}N_3NaO_3S$ abbreviated as MO, molecular weight: 327.33 g.mol⁻¹, $\lambda_{max} = 466$ nm) was purchased from Sigma Aldrich Chemicals. Table 2 gives the main properties of the MO (Trabelsi et al., 2013). Analytical grade reagents were used without prior purification.

2.2. Preparation and characterization of adsorbents

2.2.1. Preparation of the DPP

The DPP presented in Fig. 1 was produced according to two steps. Firstly, the DPP presented in Fig. 1 (A) was cleaned using the distilled water to wash the mud and dirt from its surface. The washed sample was dried at room temperature in three days. The dried DPP was ground and sieved to obtain a uniform particle size $< 2 \mu m$ (See Fig. 1 (B)), it was cleaned by distilled water and dried at 50 °C in an oven for 24 h. The low temperature was selected to avoid thermal desactivation of the surface of the date palm petioles. The DPP was then subjected to the thermal treatment.

2.2.2. Preparation of the DPB

To produce the DPB, the DPP was subjected to the thermal pyrolysis. The sample was placed in a crucible and then placed in a fixed-bed stainless steel tubular furnace under N₂ atmosphere. The temperature was raised from room temperature to 450 °C at a heating rate of 10 °C/min and sustained for 2 h. The temperature of pyrolysis was selected based on the results found by Pandey et al. (Pandey et al., 2020), they found that to target the product of biochar, the pyrolysis process must be slow under a range of temperature of 350–700 °C for 2–7 °C/min heating rate under O₂ free or limited for a per-

Process	Main characteristic (s)	Advantages		Disadvantages				
Coagulation/focculation	Uptake of the pollutants and separation of the products formed	 Process simplicity. Integrated physicochemical process. A wide range of chemicals are available commercially. Significant reduction in the chemical oxygen demand and biochemical oxygen demand. 	 Interesting reduction in total organic carbon and absorbable organic halogen (pulp and paper industry). Rapid and efficient for insoluble contaminants (pigments, etc.) removal. Inexpensive capital cost. 	 Requires adjunction of non-reusable chemicals (coagulants, flocculants, and aid chemicals). Physicochemical monitoring of the effluent. 	 Increased sludge volume generation (management, treatment, cost). Low removal of arsenic. 			
Membrane filtration	Nondestructive separation Semipermeable barrier	 Wide range of commercial membrane available from several manufacturers; large number of applications and module configurations. Simple, rapid and efficient, even at high concentrations. 	 Produces a high-quality-treated effluent. No chemicals required. Low solid waste generation. Eliminates all types of dyes, salts and mineral derivatives. 	 Investment costs are often too high for small and med- ium industries. High energy requirements. The design of membrane fil- tration systems can differ significantly. High maintenance and oper- ation costs. 	 Low throughput. Limited flow rates. Not interesting at low solute feed concentrations. Rapid membrane clogging (fouling with high concentrations). 			
Photocatalysis	Emerging processes Destructive techniques	 In situ production of reactive radicals. Little or no consumption of chemicals. Mineralization of the pollutants. No production of sludge. 	 Rapid degradation. efficient for recalcitrant molecules (dyes, drugs, etc.). Very good abatement of chemical oxygen demand and total oxygen demand. 	 Laboratory scale. Economically non-viable for small and medium industries. Technical constraints. 	Formation of by-products.Low throughput.			
Ion exchange	Nondestructive process	 Wide range of commercial products available from several manufacturers. Technologically simple (simple equipment). Can be applied to different flow regimes. 	 High regeneration with possibility of external regeneration of resin. Well-established and tested proce- dures; easy control and maintenance. 	 Economic constraints (initial cost of the selective resin, maintenance costs, regeneration time-consuming, etc.). Large volume requires large columns. 	• Saturation of the cationic exchanger before the anio- nic resin (precipitation of metals and blocking of reactor).			
Chemical oxidation	Use of an oxidant (e.g., O ₃ , Cl ₂ , ClO ₂ , H ₂ O ₂ , KMnO4	 Integrated physicochemical process. Simple, rapid and efficient process. Generation of ozone on-site (no storage-associated dangers). 	 Quality of the outflow (effective destruction of the pollutants and efficient reduction in color). Good elimination of color and odor (ozone).Efficient treatment for cvanide and sulfide removal. 	 Chemicals required. Production, transport and management of the oxidants (other than ozone). Pre-treatment indispensable. 	 Short half-life (ozone). A few dyes are more resistant to treatment and necessitate high ozone 			
Adsorption	Nondestructive process Use of a solid material	 Technologically simple (simple equipment) and adaptable to many treatment formats. Wide range of commercial products. Wide variety of target contaminants (adsorption). 	 Excellent ability to separate a wide range of pollutants, in particular refractory molecules (CAC is the most effective material). Highly effective process (adsorption) with fast kinetics. Excellent quality of the treated effluent. 	Relatively high investment.Cost of materials.Nondestructive processes.	 Non-selective methods. Performance depends on the type of material. 			

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Table 2 The main properties of the MO dye.									
Molecule	Formula	Structure	Molecular weight	Molecular size					
Methyl orange MO	$\mathrm{C}_{14}\mathrm{H}_{14}\mathrm{N}_3\mathrm{NaO}_3\mathrm{S}$	$ \begin{array}{c} & & & \\ & & & $	327,33	1.19 nm $ imes$ 0.67 nm $ imes$ 0.38 nm					



Fig. 1 A) Date palm petioles used in this study; B) Date palm petiole particles after crushing and sieving (particle size $< 2 \mu m$).

iod of pyrolysis. The biochar was sealed in an airtight jar for further use and it is further herein abbreviated as "DPB".

2.2.3. Characterization

The Fourier transform infrared analysis (FTIR) of DPP and DPB was recorded between 4000 and 400 cm⁻¹ at 32 scans using Thermo Nicolet Nexus 8700 model (Thermo electron, Madison USA) to examine the changes in functional groups on the prepared materials.

The surface morphology of DPP and the biochar DPB were analyzed with Zeiss sigma HDVP (Carl Zeiss GmbH, Oberkochen Germany) scanning electron microscopy (SEM). Separate voltages and magnifications were chosen to optimize the image. Samples for the analysis were sputtered with gold by using agar auto gold sputter.

The point of zero charge is the pH where the positive charges on the adsorbent surface equals the negative charges. If the pH of the solution is lower than the pH_{PZC} of the adsorbent, the surface functional groups of the adsorbents will be protonated by an excess of H^+ protons and the support becomes an anion exchanger. If the pH of the solution is higher than pH_{PZC} , the surface functional groups will be deprotonated by the presence of OH^- ions in the solution and the adsorbent then becomes cation exchanger. To determine the point of zero charge, the method described by Nandi et al. (Nandi et al., 2009) was used. This method consists in adding 20 mg of adsorbent to 20 mL of distilled water at dif-

ferent pH ranging from 2 to 12 (The pH was adjusted using 0.1 M HCl and NaOH solutions). The suspension is then stirred for 24 h, at the end of which its final pH (pH_f) is measured. The point of zero charge is determined by plotting pH_{j} - pH_{i} as a function of pH_{i} . The point of tangency to the curve and parallel to the pH axis, gives the value of pH_{PZC}.

2.3. Adsorption studies

2.3.1. Effect of initial concentration, pH solution and temperature on adsorption of MO onto DPB

Batch adsorption experiments were performed to investigate the MO dye adsorption. A solution of 1000 mg. L^{-1} (stock) was prepared and covered to prevent photo-degradation. Dilution was used to prepare different concentrations of the dye (50–1000 mg. L^{-1}) from the stock solution.

10 mg of DPB and a volume of 10 mL from a range of initial concentration of MO of 50–150 mg.L⁻¹ at pH 4 and at room temperature (24 \pm 1 °C) were put in erlen meyer (50 mL) and were agitated at 200 rpm on a shaker until equilibrium time. After that, solutions were filtered and the dye residual concentrations of all batch adsorption experiments were analyzed with UV–VIS Spectrophotometer (UV-1700 spectrophotometer) at $\lambda_{max} = 466$ nm wavelength. The adsorbed MO capacities on the DPB at equilibrium were calculated using Eq. (1) and the percentage removal efficiency was determined according to Eq. (2):

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

$$R (\%) \frac{(C_i - C_e)}{C_i} \times 100 \tag{2}$$

Where C_i and C_t (mg.L⁻¹) are the initial and the residual concentrations at each time *t*, respectively. *V* is the volume of the MO solution (L) and *m* is the mass of adsorbent used (g).

The effect of initial pH on the adsorption of MO onto the biochar was investigated at room temperature 24 ± 1 °C using an initial concentration of the dye of 100 mg.L⁻¹ in a range of 4–12. The pH value was adjusted by adding a few drops of 0.1 M NaOH or HCl before each experiment. The measurements were done by a pH-meter. Experiments were carried out using 10 mL of dye solutions with 10 mg of DPB. The suspensions were stirred until equilibrium time, then filtered and analyzed with UV–VIS Spectrophotometer at $\lambda_{max} = 466$ nm wavelength.

The effect of temperature on the MO adsorption onto DPB was investigated to determinate the nature of the process. A volume of 10 mL of 100 mg.L⁻¹ of MO solution at non adjusted pH was added to 10 mg of DPB. Solutions were stirred at 293, 303, 313, and 323 K temperatures until the equilibrium time, and then residual MO concentrations were analyzed in the UV–Vis spectrophotometer.

2.3.2. Isotherm study

Adsorption isotherm studies were investigated in a range of initial MO concentration from 50 to 1000 mg.L⁻¹ to find the adsorption capacity on DPP and DPB. The amount of adsorbent (10 mg) was added to 10 mL of determined MO concentration at natural pH and at room temperature (24 ± 1 °C) and stirred until equilibration time. The solution was filtered, and the dye residual concentrations of all batch adsorption experiments were analyzed with UV–VIS Spectrophotometer at $\lambda_{max} = 466$ nm wavelength. The adsorbed MO capacities

on the DPP and on DPB at equilibrium time were calculated using Eq. (1) and the percentage removal efficiency was determined according to Eq. (2).

2.3.3. Reusability study

In order to make the adsorption low cost process, the prepared adsorbent must be reused for further cycles. The reusability study of DPB was carried out with the same conditions as the adsorption kinetics. An initial concentration of MO of 100 mg.L⁻¹, a mass equal to 100 mg of adsorbent and a 100 mL volume of dye solution was used for adsorption and possibly saturation of the adsorbent with the dye. For the desorption of MO, the study was carried out using 100 mL of 0.1 M sodium hydroxide solution, the solution was stirred for 24 h. After which the solution was analyzed using a UV-Vis spectrophotometer at 466 nm. Once the dye have been desorbed, the DPB was washed several times with distilled water; air dried and then reused for readsorption at room temperature (24 \pm 1 °C). The adsorption–desorption of MO was carried out for three cycles. The percentage of desorption of MO was calculated using the following equation :

$$R(\%) = \frac{q_{des}}{q_{ads}} \times 100 \tag{3}$$

3. Results and discussion

3.1. Characterization

3.1.1. Fourier transform infrared analysis

FTIR spectroscopy was used in order to determine the presence of different functional groups on the surface of adsorbents. Infrared spectra of adsorbents based on date palm petioles: DPP, DPB are given in Fig. 2. The DPP spectrum shows a moderately intense and wide band between 3300 and 3600 cm^{-1} corresponding to the vibrations of elongation of hydroxyl groups OH (carboxylic, phenolic or alcohol groups)



Fig. 2 The Fourier transform infrared analysis of DPP and DPB.

and adsorbed water. The spectra shows adsorption bands between 2970 and 2880 cm⁻¹ resulting mainly from the vibrations of elongation of C–H of the aliphatic molecules. The band around 1626 cm⁻¹ corresponds to the valence vibrations of the C = O bands of the carboxylate groups. The 1068 cm⁻¹ band is attributed to the valence vibrations of the C-O band of the phenolic groups. The bands between 1000 and 1300 cm⁻¹ are assigned to the strain vibrations of C-O bonds (Khadhri et al., 2019). A disappearance of the intensity of all peaks on the spectra of the DPB is noticed, this results is due to the decomposition of the structure of DPP by the thermal treatment.

3.1.2. Scanning electron microscopy analysis

Scanning electron microscopy (SEM) is a widely used technique to characterize the morphology, topology, and detailed surface structure of solid materials. The SEM images of DPP and DPB are given in Fig. 3.

The surface of DPP is relatively smooth with the appearance of pores as shown in Fig. 3. DPB scanning electron microscopy image demonstrate that there are small cavities, cracks joining the fine particles of the adsorbent, forming a complicated pore network system. The roughness of the surface of the DPB is shown in Fig. 3 which suggests a porous structure on the surface of the biochar. The formation of the porous structure is due to the decomposition of the structure of DPP. This porosity increases the adsorption efficiency on the adsorbents by creating more active sites.

3.1.3. Point of zero charge analysis

The pH is a very important parameter in determining the mechanism of adsorption. For this reason, it is important to know the point of zero charge of the adsorbent. The presence of H^+ and OH^- ions in the solution can change the charge potential of the surface of adsorbents. The results obtained are shown in Fig. 4. The curves shows that the pH_{PZC} of DPP and DPB is 5.49 and 8.25, respectively, for the values of pH < pH_{PZC} (pH < 5.49; and pH < 8.25), adsorbents are attractors of negatively charged adsorbate and for the pH > pH_{PZC} (pH > 5.49; and pH > 8.25), adsorbents are



Fig. 4 pH_{PZC} of DPP and DPB.

attractors of adsorbate positively charged. The difference in the pH_{PZC} values of DPP and DPB is owing to the pyrolysis treatment, The surface composition determined by FTIR analysis confirms that greater quantities of carbonyl and carboxyl groups are formed on biochars. The formation of these functional groups contributes to add negative charges on the surface and consequently the pH at the point of zero charge increases for the biochars. Similar results were found by suliman et al. (suliman et al., 2016).

3.2. Batch methyl orange adsorption studies

3.2.1. Effect of initial concentration and contact time on methyl orange removal

Kinetic study describes the reaction rates that determine the contact time required to reach the adsorption equilibrium. It is an important parameter in any adsorption study. MO adsorption kinetic on DPB was performed using three different initial concentrations (50, 100 and 150 mg.L⁻¹) in order to predict the equilibrium time and to investigate the effect of the ini-



Fig. 3 Scanning electron microscopy of DPP and DPB.



Fig. 5 Effect of MO initial concentration and contact time on the adsorption.

tial MO concentrations and contact time on its uptake. The results of MO kinetics study are given in Fig. 5. Fig. 5 shows that MO adsorption is very fast from the first minutes followed by a slow step until reaching equilibrium after 40 min for initial concentrations of MO 50 and 100 mg.L⁻¹, and after 60 min for initial MO concentration of 200 mg.L⁻¹. The fast adsorption of MO molecules on the DPB is owing to the great affinity between the positive charge of the biochar and the negative charge of dve molecules, in addition, free actives sites in the surface of DPB at the beginning of the adsorption process leads to fast adsorption. The 200 mg.L⁻¹ initial MO concentration was reached a little long compared to the first two concentrations (50 and 100 mg. L^{-1}). This can be explained as follows: in the first minutes the existence of easily accessible sites, probably located on the external surfaces of the supports (Aichour and Zaghouane-Boudiaf, 2020), followed by molecular diffusion of the dye towards the less accessible adsorption sites before reaching an equilibrium of adsorption where all sites become occupied, so probably the competition between the molecules made the equilibrium time much longer (Zaghouane-Boudiaf and Boutahala, 2011). The effect of the initial concentration of MO on the adsorption process is shown clearly, the increase in the initial concentration of the dye leads to an increase in its uptake.

3.2.2. Kinetic modeling

It is very important to know the rate and the mechanism by which the pollutant is removed. For this, three kinetics models were applied to assess the adsorption parameters, the pseudo-first-order model (Lagergren, 1898) (Eq. (4)), the pseudo-second-order model (Ho and McKay, 1999) (Eq. (5)), and the intraparticle diffusion model (Weber and Morris, 1962) (Eq. (6)).

$$q_t = q_e (1 - e^{-k_1 t})$$
 (4)

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{5}$$

$$q_t = k_i t^{1/2} + C \tag{6}$$

Where, q_t is the amount of adsorbed MO per unit mass of DPB at time t (mg.g⁻¹), qe is the amount of adsorbed MO per unit mass of DPB when equilibrium is reached (mg.g⁻¹), k_I is a pseudo-first-order rate constant (min⁻¹), and k_2 is a pseudo-second-order rate constant (g.mg⁻¹.min⁻¹), ki is a intraparticle diffusion rate constant (mg.g⁻¹.min^{1/2}), C is the intersection of the line with the ordinate axis. The value of C gives an idea about the thickness of the boundary layer.

In order to show the effectiveness of the applicability of the kinetic and the isotherm models in the modeling of the experimental data, the correlation coefficient R^2 and the error coefficients (Residual root mean square error (RMSE) have been used. The R^2 and RMSE can be determined by the following equations:

$$\mathbf{R}^{2} = 1 - \frac{\sum_{n=1}^{n} (\mathbf{q}_{e.exp.n} - \mathbf{q}_{e.eal.n})^{2}}{\sum_{n=1}^{n} (\mathbf{q}_{e.exp.n} - \mathbf{q}_{e.exp.n})^{2}}$$
(7)

$$RMSE = \sqrt{\frac{1}{n-1} \sum_{n=1}^{n} (q_{e.exp.n} - q_{e.cal.n})^2}$$
(8)

The model plots of pseudo-first-order and pseudo-secondorder are given in Fig. 6, the results are given in Table 3.

According to the results given in Table 3, the pseudosecond-order model describes better the adsorption kinetics of MO on DPB, because the correlation coefficients of this model are bigger compared to those of pseudo-first-order model as well, the values of the adsorbed quantities found by these model are very close to the experimental values. Similar results were found by Gülen and İskeçeli (Gülen and İskeçeli, 2017).

For the model of intraparticle diffusion, which is the most commonly used technique to identify the mechanisms involved in adsorption, from the experimental data and in particular from the plot of the amount adsorbed as a function of time^{0.5} presented in Fig. 7 and the kinetics parameters of the intra-



Fig. 6 Kinetics modeling using pseudo-first-order and pseudo-second-order models.

Pseudo-first-order			Pseudo-second-order							
C ₀ (mg.L ⁻¹)	q _{exp} (mg.g ⁻¹)	K ₁ (min ⁻¹)	q _{e,cal} (mg.g ⁻¹)	R ²	RMSE	K ₁ (min ⁻¹)	q _{e,cal} (mg.g ⁻¹)	h (mg.g ⁻¹ .min ⁻¹)	R ²	RMSE
50	37.71	0.128	36.83	0.984	2.179	0.004	39.03	6.093	0.999	34.86
100	65.12	0.485	63.94	0.931	294.74	0.013	65.83	56.33	0.984	66.96
150	118.93	0.136	115.74	0.970	597.69	0.001	123.38	15.22	0.987	264.05





Fig. 7 Kinetics modeling using intraparticle diffusion model.

Table 4Parameters of intraparticle diffusion of MO adsorption on DPB.

	Step 1		Step 2				
$C_0 (mg.L^{-1})$	Ki (mg.g ⁻¹ .min ^{-1/2})	\mathbf{R}^2	Ki (mg.g ⁻¹ .min ^{-1/2})	\mathbf{R}^2			
50	8.679	0.971	0.188	0.454			
100	7.464	0.934	0.141	0.24			
150	15.409	0.925	0.454	0.30			

particle diffusion model are shown in Table 4, the curves are linear if intraparticle diffusion is involved in the phenomena of binding of the adsorbed element. Moreover, if this line passes through the origin, then the rate of intraparticle diffusion is the limiting step of the interaction. In our case, we notice that all adsorbents have two parts of intraparticulate diffusion which are linear, the first region can be attributed to intraparticle diffusion and the second region corresponds to adsorption equilibrium. We see that there is an intraparticle diffusion but this is not the dominant step in the process, it can occur at the same time in pseudo-second-order kinetics. Same results were found by Gülen et al. (Gülen et al., 2017).

3.2.3. Effect of pH

The influence of pH on the adsorption of MO on DPB was studied at an initial concentration of 100 mg. L^{-1} . The results



Fig. 8 Effect of pH on the adsorption of MO on DPB.

are given in Fig. 8. Fig. 8 shows that there is a very slight variation in the values of the adsorbed amounts depending on the pH of MO. As shown the Fig. 8, the maximum adsorbed amount of MO was found to be at pH 4, then, it was decreased with the increase of the pH until the value 10, after, it remains constant in the range of pH 10–12. Similar results were found by Oussalah et al. (Oussalah et al., 2019)

The dissociation constant pKa of MO is 3.46. The MO molecules species are the predominant in solution when pH < pKa, whereas the ionic species MO⁻ predominate in solution when pH > pKa (pKa of MO is 3.46). The uptake decreased with the increase of solution pH indicating that high pH is not in favor of the adsorption of MO because of the competition between OH⁻ excess in the solution and anionic ions of MO.

The highest removal of MO in acidic medium is mainly due to the strong attraction between the H^+ and MO⁻ ions. While in basic medium, MO removal is lower due to the competition of OH⁻ ion with MO⁻ ions for the same active sites of the adsorbent. Same results was found by Zubair et al. for the effect of pH on MO adsorption using biochar-derived date palm fronds waste (Zubair et al., 2020).

3.2.4. Effect of temperature

Temperature is a very important parameter in the adsorption phenomenon. It has two main effects; it increases the diffusion rate of adsorbate molecules through the boundary layer outside and inside the pores of the adsorbent particles, because of the decrease in solution viscosity (Nandi et al., 2009), and, it increases the solubility of adsorbate (Bartell et al., 1951; Hameed, 2007).

To observe the effect of temperature on the adsorption of MO on DPB, the experiments were employed at different temperatures 293, 303, 313, and 323 K.

The thermodynamic characteristics of the adsorption experiments were analyzed using the following equations (Acemioglu, 2004; Homaeigohar et al., 2016; Lee et al., 2020).

$$\Delta \mathbf{G}^{`} = \Delta \mathbf{H}^{`} - \mathbf{T} \Delta \mathbf{S}^{`} \tag{9}$$

$$\Delta G^{\circ} = -RTln(K_e) \tag{10}$$

$$ln(K_e) = \frac{\Delta S'}{R} - \frac{\Delta H'}{RT}$$
(11)

$$(K_e) = \frac{q_e}{C_e} \tag{12}$$

Where ΔG° is the change in Gibb's free energy (kJ.mol⁻¹), ΔS° is the change in entropy (J.mol⁻¹.K⁻¹), ΔH° is the change in enthalpy (kJ.mol⁻¹), R is the ideal gas constant (J.mol⁻¹. K⁻¹), K_e is the equilibrium constant. ΔS° and ΔH° are obtained from the relationship between $\ln(K_e)$ and 1/T in Eq. (11).

The plot of $\ln(Ke)$ versus 1/T is illustrated in Fig. 9, where ΔH° and ΔS° can be calculated by the slope and intercept of



Fig. 9 Effect of temperature on the adsorption of MO on DPB.

 Table 5
 Thermodynamic parameters of MO adsorption on

DPB.			-
Temperature (K)	ΔG ⁰ (kJ.mol ⁻¹)	ΔH ⁰ (kJ.mol ⁻¹)	ΔS^0 (J.mol ⁻¹ . K^{-1})
293	-19.77		15.93
303	-19.93	-15.10	
313	-20.09		
323	-20.25		

the given line. ΔG° was obtained using Eq. (9). The values of ΔH° ; ΔS° and ΔG° are listed in Table 5. The values of the free energy (ΔG°) at different temperatures are negatives and increase with increasing temperature; these values show that the adsorption is spontaneous and favorable at high temperatures (Mondal et al., 2015).

The negative value of ΔH° (-15.10 kJ.mol⁻¹) indicated that the adsorption is exothermic. Positive value of ΔS° (15.93 J.mol⁻¹K⁻¹) indicates that the randomness at the solution/adsorbent interface increased during the adsorption process (Oussalah et al., 2019; Gülen and Zorbay, 2017; Gülen and Aslan, 2020).

3.2.5. Equilibrium study

Adsorption isotherm study is very useful for understanding the mechanism of adsorption. In general, adsorption isotherm provides information on adsorbent optimization and design, a description of the affinity and binding energy between the adsorbate and the adsorbent, and the adsorption capacity. All this information can be extracted from equilibrium models describing the adsorption process. The isotherm also allows hypotheses to be made on the mode of adsorption. Indeed, its appearance is representative of certain phenomena involved: adsorption in monolayer or multilayer, lateral interactions between molecules or not (Qiuhong et al., 2007).

The MO adsorption isotherms on DPP and DPB are represented in Fig. 10. Both isotherms have a similar appearance. They show that when the initial concentration of MO increases, the adsorbed quantity increases up to a level indicating the saturation of all active sites on the surface of the adsorbent, which shows that the MO adsorbs homogeneously using ionic interactions provided by the surface of the adsorbent, negatively charged. These isotherms are type L according to the Gilles classification, characterized by the strong interaction between the adsorbed molecules and the surfaces of the adsorbent.

The adsorbed amounts of MO on the DPP and DPB are 227.20 and 461 mg.g⁻¹ respectively. By comparing between the isotherms, it appear clearly the great affinity of the two adsorbents with MO since the surface of the adsorbents is pos-



Fig. 10 Isotherm study of MO adsorption on DPP and DPB.



Fig. 11 Isotherms modeling graphs of MO adsorption on DPP and DPB.

itively charged, while the charge of MO dye is negatively charged, therefore, there is probably an electrostatic attraction between the charges which makes the adsorption favorable. The high adsorption removal of MO dye found on DPB (461 mg.g⁻¹) in comparison with the same found on DPP (227.20 mg.g⁻¹) can be justified by the creation of pores through the thermal treatment and the decomposition of the structure of the DPP, which prove the effectiveness of the therA. Aichour et al.

mal treatment of DPP on MO adsorption process justified by the Scanning electron microscopy analysis shown in Fig. 3.

3.2.6. Isotherm modeling

The results of isothermal adsorption of MO onto DPP and DPB experiments were analyzed using the nonlinear form of Langmuir (Langmuir, 1918) (Eq. (13)), Freundlich (Freundlich, 1906) (Eq. (14)), and Temkin (Temkin et al., 1940) (Eq. (15)) models.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{13}$$

$$q_e = K_F C_e^{1/n} \tag{14}$$

$$\boldsymbol{q}_{\boldsymbol{e}} = \boldsymbol{B}\boldsymbol{l}\boldsymbol{n}(\boldsymbol{A}\boldsymbol{C}_{\boldsymbol{e}}) \tag{15}$$

Where C_e is the concentration of MO in the aqueous solution at equilibrium (mg.L⁻¹), K_L is the Langmuir adsorption constant (L.mg⁻¹) related to the binding energy, q_m is the maximum adsorption amount (adsorption capacity in mg.g⁻¹), K_F is the distribution coefficient (L.g⁻¹), n is the Freundlich constant, and A, B are Temkin constants.

The best model among those which we choose is evaluated starting from the value of R^2 , the value of *RMSE*, and the maximum adsorbed quantity which must be similar to the experimentally found.

The isotherm modeling is given in Fig. 11. And the results are given in Table 6. According to the results of the Table 6, The experimental data yielded good fits with in the following isotherms order: Langmuir > Temkin > Freundlich. the

Table 6	able 6 Isotherms modeling parameters of MO adsorption on DPP and DPB.												
A	q _{max} ,exp	_{xp} Langmuir				Freundlich				Temkin			
	(mg.g ⁻¹)	q _{max} (mg.g ⁻¹)	K _L (L.mg ⁻¹)	R ²	<i>RMSE</i> (10 ⁵)	1/n	K _F	R ²	RMSE (10 ⁵)	A	В	R ²	$\begin{array}{c} \mathbf{RMSE} \\ (10^5) \end{array}$
DPP DPB	227.20 461	256.27 514.79	0.017 0.032	0.841 0.850	0.124 0.582	0.294 0.241	38.48 109.8	0.746 0.701	0.200 1.160	0.164 0.403	55.149 94.879	0.802 0.774	0.156 0.877

 Table 7
 Comparison of monolayer MO adsorption onto various adsorbents with DPP and DPB.

Adsorbents	pН	Temperature (°C)	Maximum monolayer adsorption capacities (mg.g ⁻¹)	References
Date Palm Petioles (DPP)	4	24 ± 1	227.20	This study
Date Palm Petioles derived Biochar (DPB)	4	24 ± 1	461	This study
Calcined Lapindo volcanic mud	3	/	333.3	Jalil et al., 2010
Hexagonal shaped nanoporous carbon	/	25	18.8	Kundu et al., 2017
Ferric oxide–biochar nano-composites derived from pulp and paper sludge	8	25	20.53	Chaukura et al., 2017
Biochar-derived waste biomass	/	/	306.13	Caglar et al., 2018
Carboxymethyl cellulose (CMC) biochar	6.5	25 ± 1	39.47	Yu et al., 2018
Amino functionalized Zr-based MOFs	5	25	148.4	Lv et al., 2019
ZnO/polyaniline nanocomposite (ZnO-PANI-NC)	4	/	240.84	Deb et al., 2019
Corn cob biochar	5.6	25	86.38	Zhang et al., 2020
Activated biochar derived from pomelo peel wastes	3	25	163.10	Zhang et al., 2020
Biochar-derived date palm fronds waste	4	25	163.132	Zubair et al., 2020
Pine cone biochar activated with KOH	2	25	160	Kaya and Uzun, 2021



Fig. 12 Reusability study of DPB.

model of Langmuir give very satisfactory results with a coefficient $R^2 > 0.851$ and $R^2 > 0.858$ for DPP and DPB, respectively. The maximum adsorption capacities found by these models are of 256.66 and 503.44 mg.g⁻¹ for Langmuir model respectively, which indicates that the MO adsorption process is monolayer and homogenious in nature.

Table 7 gives a comparison of monolayer MO adsorption onto various adsorbents found in literature with DPB. The biochar have shown a high adsorption capacity in comparison with the other studies.

3.2.7. Reusability study

To consider a matter as a promising adsorbent, it must have significant properties such as high adsorption capacity, the ability to be regenerated and therefore to be reused several times in the process. Adsorbent with these characteristics is considered cost effective and applicable on an industrial scale. The result of the reusability of DPB is shown in Fig. 12. As given in this figure, it appears that the chosen 0.1 M sodium hydroxide solution as desorbing agent of MO has shown a very good results. The removal percentage of MO from the DPB was calculated through three adsorption-desorption cycles, it was found to be 81.03 %, 67.84 %, and 51.72 %, respectively, a slight decrease in the ability of MO adsorption has noticed with the increase of the number of adsorption-desorption cycles. The decrease in the performance of adsorption might be due to the repulsion between the negative charge of MO⁻ molecules and the deprotonated surface of the adsorbent by OH⁻ ions under basic medium.

4. Conclusion

The Date palm petioles have been chosen in the present study due to their remarkable properties to prepare biochar used for to removal of MO dye from wastewater. The adsorption studies was applied in batch mode according to many parameters such as initial dye concentration, equilibrium time, pH of the solution and the temperature. Equilibrium was studied for the comprehension of the mechanism of adsorption. Reusability study of DPB was investigated and the results has proven the possibility of the reuse of the prepared biochar for three cycles of adsorption–desorption.

Biochars prepared from biomass are abundant, very simple in preparation, low-cost, biodegradable, has bioremediation of dye solutions and gives very satisfactory results in the removal of pollutants from wastewater.

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