

Removal of cationic dye by high surface activated carbon prepared from biomass (date pits) by carbonization and activation processes

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Abstract

In this work, we investigated the capacity of activated carbon (AC) to adsorb Methylene Blue (MB) from aqueous solution. AC-H₃PO₄ and AC-ZnCl₂ was obtained from date pits via a one-step chemical method using H₃PO₄ and ZnCl₂ as activating agents. The performance of AC was characterized by different analyses techniques: proximate analysis, SEM, XRD and FT-IR and TGA. The experiments results showed that the MB removal increased by increasing each of AC-H₃PO₄ and AC-ZnCl₂ concentration, contact time and temperature. The efficiency of the adsorption tests are evaluated by the Langmuir and Freundlich isotherm models. Equilibrium data fitted well by Freundlich model with a maximum of the adsorption capacity of 95 mg/g at 333 K for AC-ZnCl₂. However, the adsorption was well adapted to the Langmuir isotherm with a maximum of the adsorption capacity of 125 mg/g at 298 K for AC-H₃PO₄. The kinetics data was explained by the pseudo second-order model, and the intra-particle diffusion with some other rate controlling steps has been suggested as the adsorption mechanism. The pseudo-second-order model described better the adsorption process. The thermodynamic study suggested that MB adsorption on AC-ZnCl₂ was endothermic, spontaneous and non-spontaneous for AC-H₃PO₄.

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1. Introduction

Potential surface water and groundwater resources are increasingly contaminated by different micro pollutants. Over the course of history, overall water availability has remained more or less constant. 2,000 years ago, 200 to 300 million people on earth used available resources. Today, more than 6.5 billion humans have to content themselves with the same amount of water [1]. This is why the raw material water, for a long time freely available in many parts of the earth, is today seriously threatened. In addition, the natural systems of purification of our planet are considerably overloaded. Adsorption by activated carbon (AC) is generally considered to be one of the most effective methods of controlling organic contaminants in water. Low-cost, high-carbon materials, such as agricultural by-products, residues, wood chips or wastes can be used as precursors in activated carbon production [2–5]. The physical and chemical properties of activated carbon depend on the precursor materials and preparation methods used. Nowadays, biomass has increasingly attracted attention as precursors for the preparation of activated carbon due to its high efficiency, low operating cost, chemical sludge minimization and biosorbent regeneration [6,7]. Activated carbons have been produced from different biomass [8–12]. Generally, physical and chemical activation techniques are suitable to prepare activated carbon [13,14]. Physical activation involves carbonization of raw materials at high temperatures in an inert atmosphere followed by oxidation treatment with steam, air, or CO₂ [15]. Chemical activation involves impregnation of the raw materials with chemical agents including phosphoric acid [16], sulfuric acid [9], KOH [17], NaOH [18], and ZnCl₂ [19–21]. In recent years, the adsorption technique has demonstrated a simple and cost-effective knowledge in terms of energy requirements and environmental friendliness to expel dyes from industrial wastewater, and has attracted the attention of researchers. Adsorption technique in textile dyes removal is widely investigated. using different wastes biomass are tested as adsorbent giving good performance [3,4]. For example, wheat straw has presented presents high removal efficiency of cationic dyes such as methylene blue, methyl violet and crystal violet and heavy metals [22]. The benefits associated with the use of this waste are numerous and we retain: Valorization of agro-resources as raw material available, renewable and cheap; the positive repercussion on the cost price of the turnover obtained: A certain socio-economic impact on local populations: creation of employment generating activities and, as far as possible, non-polluting. Often performed using ZnCl₂ and H₃PO₄ solutions, chemical activation is described in many studies [23–24]. Its choice may be due to its various advantages, notably [2]:

- ✓ Manipulations at low temperatures;
- ✓ The two carbonization and activation operations are combined in a single step.

The ozonation and oxidation by hypochlorite are the most effective methods of water discoloration, but, they are inadequate because of their high cost and chlorine residues resulting [25]. Numerous studies [26–29] led to the development of adsorption processes on activated carbon for the elimination of dyes, because of its effectiveness and simplicity of implementation. The aim of this work is to prepare activated carbons using a one-step chemical activation method, afterwards characterize the prepared activated carbons and finally study their adsorption efficiency to remove the MB from aqueous solution under different experimental conditions. For a better understanding of the adsorption mechanism of MB onto AC, adsorption kinetics, isotherms, and thermodynamic studies have also been performed.

2. Materials and methods

Methylene blue (MB) is the cationic dye that is most often and continuously used for dyeing cotton, wool, and silk. Therefore, wastewater produced from industries related to the use and synthesis of MB is always contaminated by this organic pollutant [30]. The molecular structure of MB is shown in **Figure 1**.

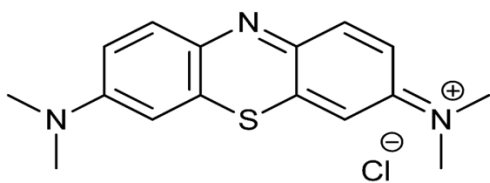


Figure 1: Molecular structure of methylene blue (MB)

2.1. Synthesis of activated carbon

The Moroccan Date Pits (MDP) was collected from Ouarzazate region in Morocco. Raw material was washed with hot distilled water to remove impurities and then dried and crushed to low particle size (about 200 μm). The impregnation process is performed by respecting ratio of MDP / $\text{MH}_3\text{PO}_4=1/2$. For activation with ZnCl_2 , 30 g of sample was dispersed in zinc chloride solution (activation mass ratio was 1:3) and stirred overnight. Both materials were carbonized at 400 $^\circ\text{C}$ for 1 h under nitrogen gas (99.99%) with a flow rate of 70 ml/min. After cooling to room temperature, the sample was washed several times with hot distilled water to remove the residual chemical activating agent. Finally, the sample was dried at 80 $^\circ\text{C}$ in a vacuum oven to obtain the activated carbon. The activated carbons prepared in this study were labeled AC- ZnCl_2 and AC- H_3PO_4 .

2.2. Characterization of the activated carbon

Thermogravimetric analysis of Moroccan date pits is carried out at the temperature range of 25-700 $^\circ\text{C}$ with the heating rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen. AC- ZnCl_2 and AC- H_3PO_4 structure was characterized by X-ray diffraction (XRD) analysis using a diffractometer with Cu-K_α radiation source ($\lambda = 1.5418 \text{ \AA}$). Also, the samples Morphology is performed using Scanning Electron Microscopy (SEM). Chemical characterization of AC- ZnCl_2 and AC- H_3PO_4 was carried out by FT-IR spectroscopy in order to identify the functional groups at the surface of carbon materials. The infrared transmission spectra were recorded from 500 to 4000 cm^{-1} . The pH of the point zero charge (pH_{PZC}) of AC- ZnCl_2 and AC- H_3PO_4 was established using the method suggested by Noh and Schwarz [31], the initial pH value is from 2.0 to 12.0 and the mass of samples used is 0.2 g.

2.3. Adsorption experiments

Batch adsorption was studied to determine the effect of pH, adsorbent dose, time, and temperature on the adsorption efficiency of AC- ZnCl_2 and AC- H_3PO_4 to remove MB. The adsorption kinetics was carried out at 25 $^\circ\text{C}$. For each experiment, 100ml of the MB solution at specified concentrations were continuously stirred with 0.1 g of the adsorbent during different time intervals (5-180 min). The effect of the initial pH of the cationic dye solution on the amount of adsorbed dye was studied at 25 $^\circ\text{C}$ over ranges of pH from 2 to 12. Experiments were conducted on suspensions of 0.1N of HCl or NaOH. The sorption kinetic studies were also carried out at different temperatures, 298K, 313K, and 333K, to determine the effect of temperature and to evaluate the sorption thermodynamic parameters. The samples were filtered to separate the adsorbent from the MB. The amount of MB remained in the solution after absorption is determined by UV-Visible spectrophotometry analysis at 664nm. The MB removal percentage and the adsorption capacity (mg / g) were calculated respectively by the equations 1 and 2, where C_0 (mg/g) is the initial concentration of MB, C_e (mg/g) is the concentration of MB at equilibrium, V (L) is the volume of the solution, and M (g) is the mass of adsorbent used.:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} * 100 \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

3. Results and Discussion

3.1. Characterization of materials

Thermogravimetric analysis of Moroccan dates (Figure 2) revealed that the initial weight loss (6.51%) at 105°C due to the release of water, followed by a second weight loss (82.45. %) around 210 to 540 °C. The evolution of light volatile compounds comes from the degradation of cellulose, hemicelluloses and lignin. The remaining weight loss (11.04%) corresponds to the mineral matter.

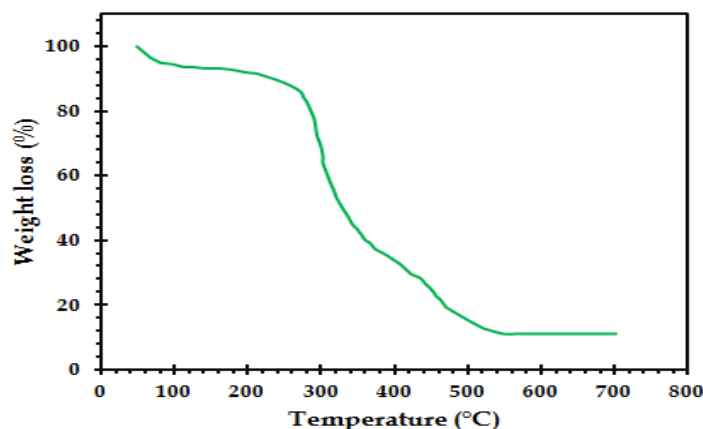


Figure 2: TGA curve of Moroccan date pits

AC-ZnCl₂ and AC-H₃PO₄ were examined by X-ray diffraction analysis (XRD). The result is shown in Figure 3, the XRD diagram shows a noisy background pattern, as commonly observed for amorphous carbon materials [32, 33]. For AC-ZnCl₂, zinc oxide (ZnO), zinc carbide and ZnC₈ peaks derived from the traces of the zinc chloride used as an activating agent. However, AC-H₃PO₄ shows a peak at $2\theta = 26^\circ$ is assigned to disordered planes (002) of graphite.

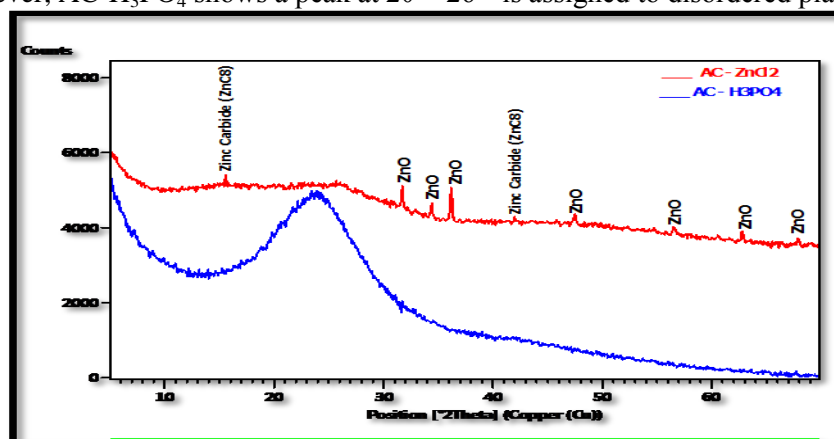


Figure III: XRD pattern of prepared activated carbons AC-ZnCl₂ and AC-H₃PO₄

The FT-IR spectra shown in Figure 4, the development of surface textures of date pits and activated carbons, according to the literature, date pits present IR band around 3400 cm⁻¹ attributed to the OH hydroxyl groups. Band around 2913 and 2844 cm⁻¹ corresponding to aliphatic CH elongation vibrations. The peak at 1737 cm⁻¹ is assigned to the carbonyl group C = O which present esters, aldehydes, ketones and carboxyl groups. Bond at 1623 cm⁻¹ characteristic of the curvature of the water, 1436 cm⁻¹ and 1482 cm⁻¹ corresponds to aromatic C = C elongation of the aromatic ring and C-H vibrations. In addition, the band at 1363 cm⁻¹ assigned to CH of cellulose or hemicellulose and 1232 cm⁻¹ correspond to CO stretching phenolic hydroxyl groups in lignin, an intense relative IR band at about 1045

cm^{-1} attributed to CO which corresponds to the elongation in acids, alcohols, phenols, ethers and esters and IR range $800\text{--}500\text{ cm}^{-1}$ attributing to the deformation ring in the plane. The FT-IR spectra of AC-ZnCl₂ and AC-H₃PO₄ showed that the majority of bands are extirpated from dates, except the bands around 3400 cm^{-1} and 1623 cm^{-1} . This is explained by the departure of most functional groups during the carbonization treatment.

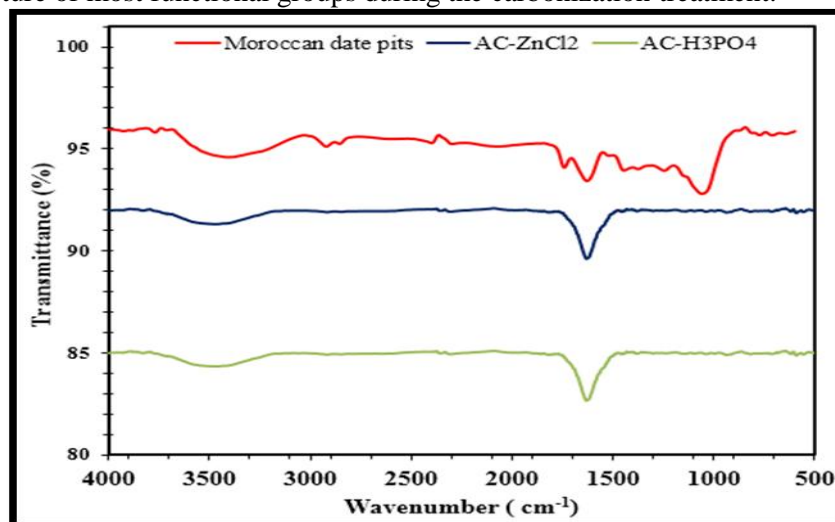


Figure IV: FT-IR spectra of date pits and activated carbons AC-ZnCl₂ and AC-H₃PO₄

The SEM images of the date pits, AC-H₃PO₄ and AC-ZnCl₂ are presented in Figure V. From these images, we observe a significant change in the morphology of the prepared activated carbons. Indeed, the impregnation with phosphoric acid and ZnCl₂ followed by pyrolysis dehydrated the cellulose material, resulting in weakening of the precursor structure and creation of pores. Phosphoric acid and zinc chloride are responsible for decomposition of organic material. This facilitates the release of volatile matter during pyrolysis process and consequently the development of the porosities. The porosities obtained can increase the surface contact between the adsorbate and the adsorbent and provide more binding sites, which facilitates the adsorption process[34].

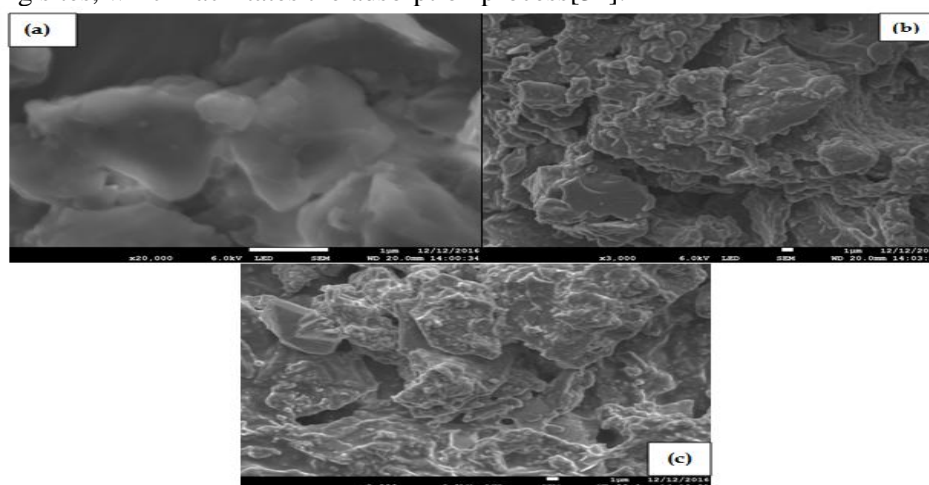


Figure 5: SEM images of (a) date pits, (b) AC-H₃PO₄ and (c) AC-ZnCl₂

3.2. Adsorption study

3.2.1. Effect of the pH on the adsorption efficiency

The effect of the pH solution on the adsorption of MB on AC-ZnCl₂ and AC-H₃PO₄ was studied at a pH range of 3 to 12 as shown in Figure 6. The MB removal percentage significantly increased when the pH of the solution increases

from 3 to 12. The nature of the activated charcoal can be acidic, neutral or basic depending on the pH_{pzc} which depends on the origin of the precursor and the preparation method (chemical or physical). Figure 7 shown that $\text{pH}_{\text{pzc}} = 7.2$ and 6.8 respectively for AC-ZnCl₂ and AC-H₃PO₄. Methylene blue is a cationic dye and provides positive ions in solutions. Thus, at $\text{pH} < \text{pH}_{\text{pzc}}$ coal is negatively charged adsorbate attractor, while the surface of the adsorbent would be surrounded by H⁺ ions, which decreases the interaction of MB ions (cationic pollutant) with adsorbent sites. On the other hand at $\text{pH} > \text{pH}_{\text{pzc}}$, the concentration of H⁺ decreases which generates a good interaction between the dye ions and the sites of the surface. The highest removal of MB was 99% and is attributed to the presence of more negative charges. Therefore, the higher pH favored MB dye adsorption [35]. Also, the adsorption of MB dye was almost constant at pH 8-12. At this stage, the surface of the prepared activated carbon can be negatively charged, thereby increasing the positively charged cationic dye by the electrostatic attraction force.

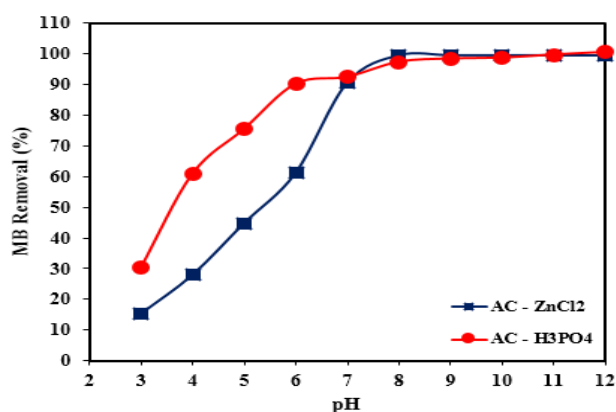


Figure 6: Effect of solution pH on MB removal by AC-ZnCl₂ and AC-H₃PO₄

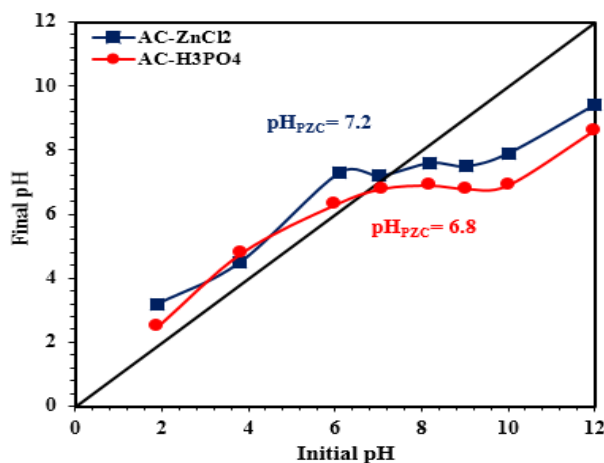


Figure 7: Point of zero charge (pH_{pzc}) of the activated carbons, determined by the pH drift method

3.2.1. Adsorbent masse effect on adsorption efficiency

The effect of the adsorbent mass of AC-ZnCl₂ and AC-H₃PO₄ on the adsorption removal of methyl bromide is illustrated in Figures 8 and 9. The mass values studied were (50 mg, 100 mg and 200 mg). Both figures show that the MB removal percentage increases as the mass of the adsorbent increases. This is easily understood because the increase in the mass of the adsorbent increases the specific surface area and therefore the number of available adsorption sites. The results also show that the MB removal percentage with AC-H₃PO₄ is almost 100%, while the MB

removal percentage with AC-ZnCl₂ does not reach 50%. For both adsorbents, the maximum adsorption is indicated for the adsorbent mass of 200 mg. This mass is fixed for other adsorption studies.

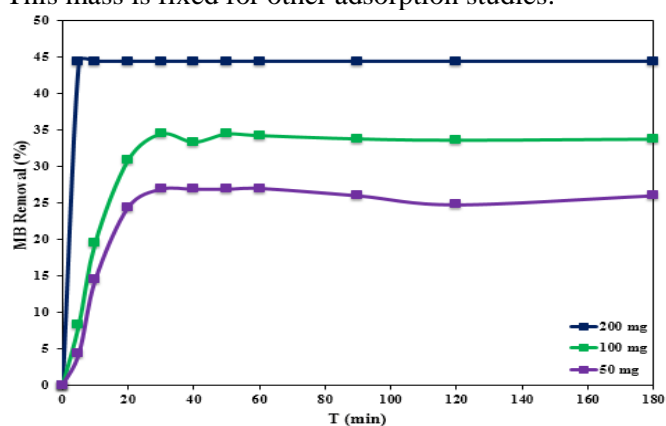


Figure 8: Effect of dose on adsorption of MB onto AC-ZnCl₂

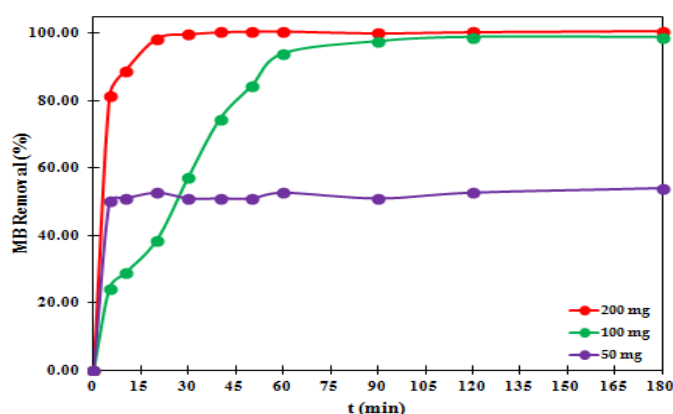


Figure 9: Effect of dose on adsorption of MB onto AC-H₃PO₄

3.2.3. Temperature effect on adsorption efficiency

The objective of this section is to study the influence of temperature - over a wide range - on AC-ZnCl₂ adsorption efficiency. For this purpose 200 mg of AC-ZnCl₂ was added to 100 ml of MB (100 mg/L) at different temperatures (298, 313 and 333 K). As showing in Figure 10, the abatement percentage of MB dye increased significantly with temperature. It's around 44% at 298 K, 50% at 313 K, and 99% at 333 K.

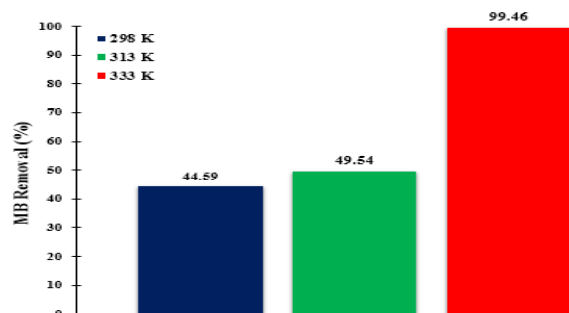


Figure 10: Effect of temperature on adsorption of MB onto AC-ZnCl₂.

This may be due to the mobility of MB molecules [35]. Furthermore, when the temperature increases, it may produce swelling effect within the internal structure of AC-ZnCl₂ allowing to the dye molecule to penetrate more [36]. Thus the temperature of 333K was fixed as an optimum for further adsorption experimental studies of AC-ZnCl₂.

3.2.3. Adsorption isotherms

In this work the adsorption isotherms are studied using Langmuir and Freundlich models, the most commonly employed in literature, details of these models are presented in Table 1 [37,38]. The Langmuir and Freundlich parameters for adsorption of MB onto AC-ZnCl₂ and AC-H₃PO₄ are determined from the corresponding plots (Figure 11a, b), which summarized in Table 2.

Table 1: Details of Langmuir and Freundlich isotherm models

Isotherm	Equation	Description
Langmuir	$\frac{1}{Q_e} = \frac{1}{(K_L Q_m)} C_e + \frac{1}{Q_m}$	C_e : concentration at equilibrium.
		Q_e : adsorption capacity at equilibrium. Q_m : maximum adsorption capacity (mg/g). K_L (dm ³ /g): Langmuir constants.
Freundlich	$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F$	K_F : Freundlich adsorption capacity (mg/g); n = intensity of adsorption; $1/n = 0$ irreversible; $1/n > 0$ unfavourable, $0 < 1/n < 1$ favourable
Dimension less factor	$R_L = (1 + K_L C_0)^{-1}$	K_L (dm ³ /g): Langmuir constant.
		C_0 : The highest initial MB concentration. The value of R_L : indicates the shape of the isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

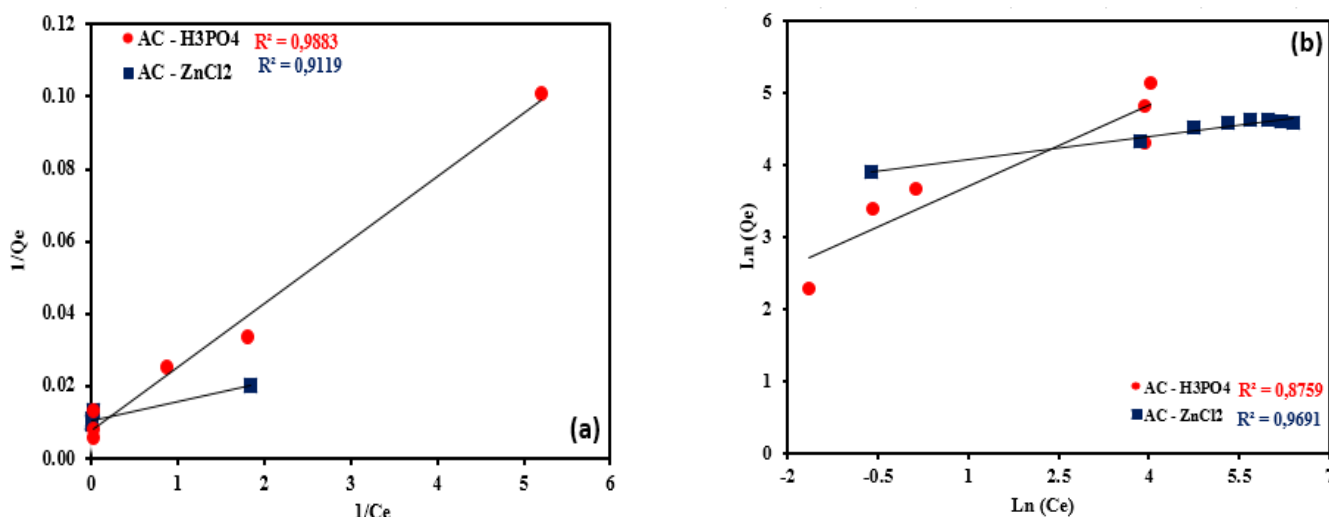


Figure 11: Langmuir (a) and Freundlich (b) isotherms for MB adsorption onto AC-ZnCl₂ and AC-H₃PO₄

From the values of R^2 shown in Table 2, it can be concluded that the Freundlich model provides a better fit for AC-ZnCl₂ as compared to AC-H₃PO₄ which is described by Langmuir model. A good fit of this isotherm indicates multilayer adsorption for AC-ZnCl₂ and monolayer adsorption for AC-H₃PO₄. However, the values of n for the Freundlich model are greater than 1 for AC-ZnCl₂ and AC-H₃PO₄, indicating that the adsorption was favorable.

Table 2: Data equilibrium of MB adsorption onto AC-ZnCl₂ and AC-H₃PO₄

Activated carbon	Langmuir				Freundlich		
	$Q_{\max}(\text{mg/g})$	$K_L (\text{L} \cdot \text{min}^{-1})$	R_L	R^2	$K_F (\text{mg/g})$	n	R^2
AC - H ₃ PO ₄	125	0.457	0.021	0.9883	28.01	2.670	0.8759
AC - ZnCl ₂	95	2.019	0.005	0.9119	53.29	9.208	0.9691

The Langmuir isotherm has been used in the determination of the specific surface area of biological and inorganic materials [38,39]. Since the Langmuir theory assumes monolayer coverage of the adsorbent's surface, the area can be calculated using physical constants[39]. The specific surface area was calculated by the following Equation[40]:

$$S_{MB} = \frac{Q_{\max} \cdot A_{MB} \cdot N \cdot 10^{-20}}{M} \quad (3)$$

where S_{MB} (m²/g) is the specific surface area; Q_{\max} (mg/g) is the maximum adsorption capacity (calculated from the Langmuir isotherm); A_{MB} is the occupied surface area of one molecule of methylene blue = 197.2 Å²[41]. N is the Avogadro's number, 6.02×10^{23} ; and M is the molecular weight of MB (373.9 g/mol). The specific surface areas of the AC-H₃PO₄ and AC-ZnCl₂ were calculated and are shown in Table 3. According to the results, AC-H₃PO₄ has the largest specific surface area (397 m²/g) compared to AC-ZnCl₂(302 m²/g).

Table 3: Specific Surface Areas determined by the methylene blue method adsorption

Activated carbon	Specific surface area (m ² /g)
AC-H ₃ PO ₄	397
AC-ZnCl ₂	302

3.3. Kinetic modeling

The kinetics of MB adsorption onto activated carbons was studied by applying pseudo-first order and pseudo-second order models [42,43], details of these models are presented in Table 4. The values of Q_e and K_1 for pseudo-first order can be determined from the intercept and slope of the linear plot of $\ln (Q_e - Q_t)$ versus t (Figure 12a). For pseudo-second order kinetics, the K_2 and calculated Q_e can be obtained from the slope and the intercept when a straight line of t/Q_t was plotted versus time(Figure 12b). Based on the results indicated in Table 5, we find that the calculated adsorption capacity ($Q_{e,cal}$)by pseudo-first-order and the experimental adsorption capacity ($Q_{e,exp}$) vary widely, unlike the pseudo-second-order model cases are very close, as the correlation coefficients are very close to 1, which further confirmed that the MB adsorption onto AC-ZnCl₂ and AC-H₃PO₄ followed the pseudo-second order kinetics, meaning the controlling rate step is chemisorption. Meanwhile, the result showed that the rate of adsorption depended on the availability of adsorption sites on the surface of AC-ZnCl₂and AC-H₃PO₄ rather than MB concentration in bulk solution.

Table 4: Kinetic models used to fit the experimental data

Kinetic model	Equation	Description
Pseudo first-order	$\ln (Q_e - Q_t) = \ln Q_e - K_1 t$	K_1 (h ⁻¹) is the rate constant. Q_t (mg.g ⁻¹) is the amount of sorption at time t (h), and Q_e (mg.g ⁻¹) is the amount of

		sorption at equilibrium.
Pseudo second-order	$\frac{t}{Q_t} = \frac{1}{K_2 Q_s^2} + \frac{t}{Q_s}$	K_2 (g.mg ⁻¹ .h ⁻¹) is the rate constant of a second order adsorption.

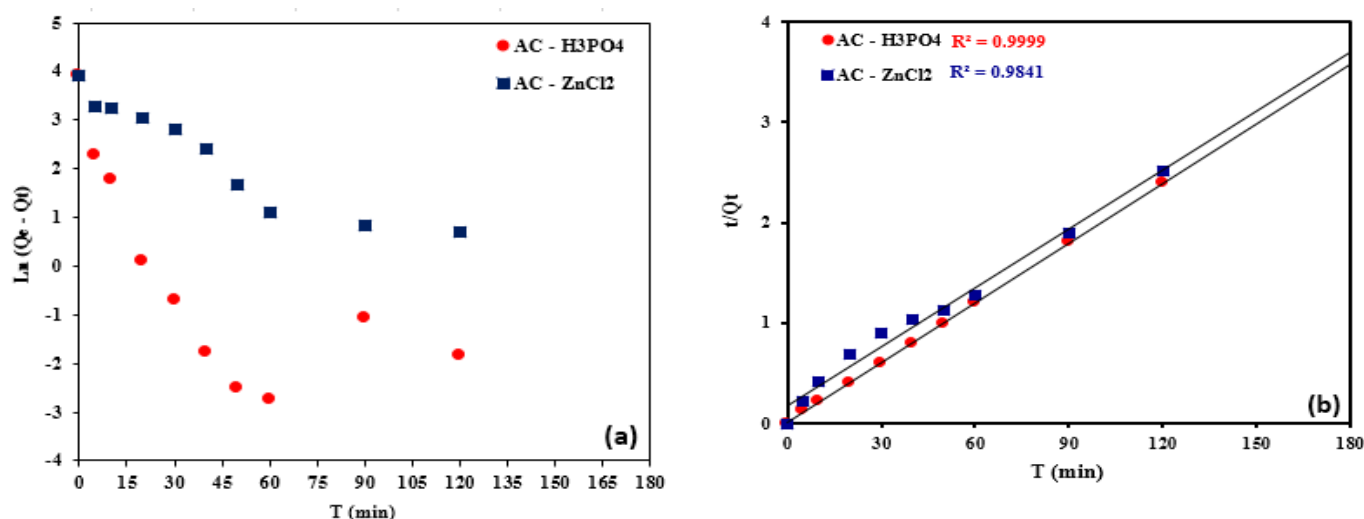


Figure 12: Pseudo-first order (a) and pseudo-second order (b) kinetics for MB adsorption onto AC-ZnCl₂ and AC-H₃PO₄

Table 5: Kinetic parameters for BPA adsorption

Activated carbon	$Q_{e,exp}$ (mg/g)	Pseudo-First-Order			Pseudo-Second-Order		
		$Q_{e,cal}$ (mg/g)	K_1 (min ⁻¹)	R^2	$Q_{e,cal}$ (mg/g)	K_2 (g/mg.min)	R^2
AC-H ₃ PO ₄	49.94	4.001	0.094	0.5279	50.50	0.034	0.9999
AC-ZnCl ₂	49.73	22.833	0.046	0.8682	53.19	0.002	0.9956

3.3.1. Intra-particle diffusion study

The diffusion mechanisms and rate controlling steps in the MB adsorption process was studied using the intra-particle diffusion model[45]. As shown in Figure 13, it is clear that the adsorption processes of AC-H₃PO₄ and AC-ZnCl₂ are divided into approximately three parts, as indicated by the guide lines for each portion [47]. The first part is attributed to the diffusion of MB molecule through solution to the external surface of AC-H₃PO₄ and AC-ZnCl₂. This is a fast process that mainly depends on the surface area of the adsorbent. The second part is attributed to the intra-particle diffusion, which is the rate-limiting stage. In the third part, the intra-particle diffusion starts to slow down and the adsorption equilibrium is established.

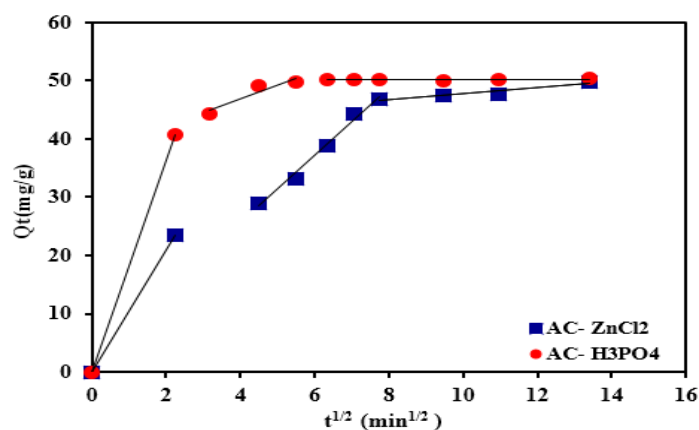


Figure 13: The plots based on the intra-particle diffusion model

As can be seen from Figure 13 the activated carbon prepared by ZnCl_2 exhibits obviously faster adsorption kinetics at the initial adsorption stage than the sample prepared by phosphoric acid due to its higher surface area. In the second and third stages, the sample AC- H_3PO_4 also shows shorter rate-limiting period for the adsorption and earlier acquirement of adsorption equilibrium than AC- ZnCl_2 .

3.3.2. Thermodynamic study

The thermodynamic parameters desired in this work were Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS), to this purpose, the Van't Hoff equation was used to determine the thermodynamic parameters [49]:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

where R (8.314 J/kmol) is the universal gas constant and T (K) is the absolute temperature;

$$K_d = \frac{Q_e}{C_e} \quad (5)$$

where K_d is the distribution coefficient; Q_e (mg/g) is the amount of MB adsorbed on the sorbent per unit mass; C_e (mg/L) is the equilibrium concentration of MB in solution when Q_e was adsorbed. The temperature range used was from 273K to 333K, a linear plot of $\ln K_d$ against $1/T$ gives a graph (Figure 14) where ΔH and ΔS were obtained from the slope and intercept respectively. ΔG was calculated using the following relation:

$$\Delta G = -RT * \ln K_d \quad (6)$$

The set of the calculated thermodynamic parameters are presented in Table 6.

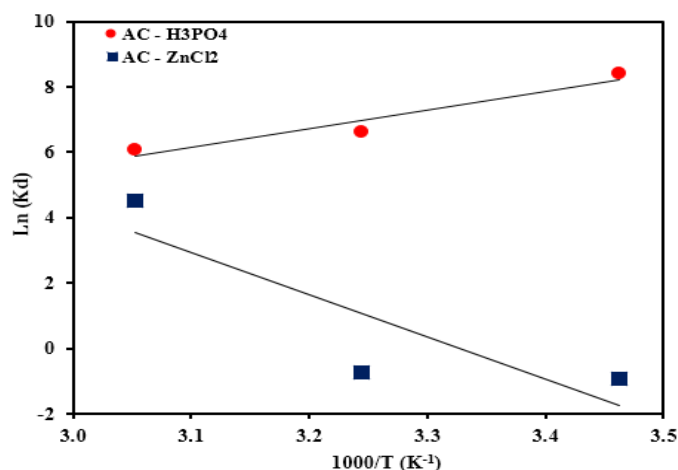


Figure 14: A plot of $\ln K_d$ against $1/T$ for MB adsorption onto activated carbons

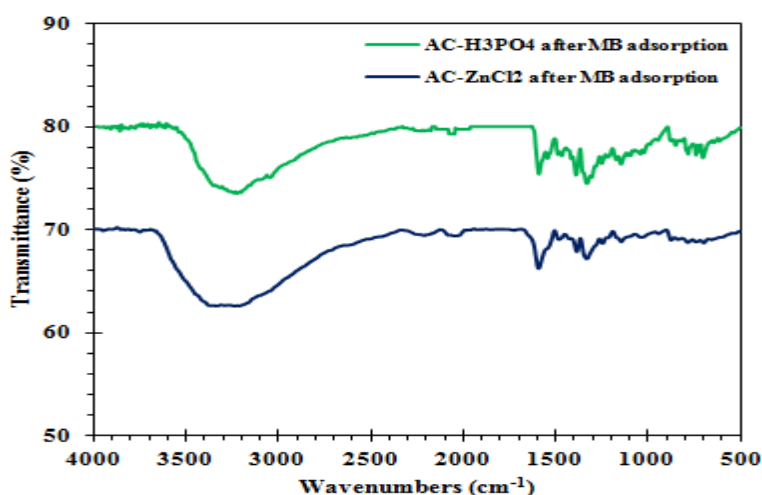
Table 6: Thermodynamic parameters for the adsorption of MB onto activated carbons

	ΔH (J/mol)	ΔS (J/mol K)	ΔG (kJ/mol)		
			293 K	313 K	333 K
AC -H ₃ PO ₄	-47	-93	27.136	28.992	30.847
AC -ZnCl ₂	108	354	-111.037	-114.830	-118.624

The positive ΔH value indicated that the sorption process on AC-ZnCl₂ is endothermic in nature and the positive value of ΔS suggests the probability of favorable adsorption which indicates the increasing randomness at the solid/liquid interface during the adsorption process. Negative values of ΔG indicate the spontaneous nature of the adsorption process. The value of ΔG becomes more negative with the increase in temperature. This shows that an increase in temperature favors the removal process. For AC-H₃PO₄ the value of ΔH was negative, indicating the exothermic processes of adsorption. The negative value of ΔS reflects the decrease in the randomness at the solid–liquid interface during the adsorption processes. The positive values of ΔG indicate that the adsorption was non-spontaneous and leads to an increase in the Gibbs free energy. Increase in the values of ΔG with increasing temperature also indicated that adsorption at lower temperature was more feasible.

3.3.3. Proposed adsorption mechanism

FT-IR analysis has been used in order to explain the adsorption mechanism of MB on prepared activated carbons. In comparison with the FT-IR spectrum of AC-H₃PO₄ and AC ZnCl₂ (figure. 4), figure 15 shown the disappearance of the peak about 1623 cm⁻¹ and the displacement of the peaks between 3400 cm⁻¹ and 3239 cm⁻¹ (OH stretch) this is probably due to the hydrogen bond between MB hydroxyl groups and activated carbons. the appearance of the new peaks at 1000-1600 cm⁻¹ after adsorption of MB on activated carbons in agreement with the peaks of the MB FT-IR spectrum, indicates the existence of a MB binding process done on surface of AC-H₃PO₄ and AC-ZnCl₂. it can be concluded that the hydroxyl groups OH, carboxyl and C-C valence of activated carbons are attacked by the characteristic peaks of methylene blue.

**Figure 15:** FT-IR spectra of AC-H₃PO₄ and AC-ZnCl₂ after adsorption of MB

4. Conclusion

Experiments of adsorption of MB have been carried out on activated carbon prepared from Moroccan date pits. Operating conditions play a vital role in all aspects of adsorption mechanism such as pH, MB concentration, activated carbon mass, temperature. The maximum abatement yield of MB occur at 333 K, pH = 8, MB concentration of 100 mg/L, 200 mg of activated carbons. The experimental results of adsorption with AC-ZnCl₂ and AC-H₃PO₄ were evaluated by the Langmuir and Freundlich isotherms. data for AC-ZnCl₂ is in agreement with Langmuir isotherm model, while AC-H₃PO₄ is in agreement with Freundlich isotherm model for. The kinetic model of pseudo-second-order corresponds very well to this dynamic adsorption. The thermodynamic calculations indicate the feasibility, spontaneity and endothermic nature of the adsorption process. Finally, the various results obtained in this work indicated that the prepared activated carbon is a promising adsorbent for wastewater treatment.

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