Experimental investigation of activated carbon prepared from apricot stones material (ASM) adsorbent for removal of malachite green (MG) from aqueous solution

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Abstract
The adsorption of malachite green onto activated carbon prepared from apricot stones material has been investigated at batch conditions. The effects of contact time (0–60 min), initial pH (3–11), agitation speed (100–700 r/min), temperature (298–343 K), adsorbent dose (1–10 g/L), and malachite green concentration (4.45–17.6 mg/L) on the malachite green adsorption by apricot stones material have been studied. Malachite green removal increases over the contact time until equilibrium. The batch adsorption experiments were carried out to optimize the physical parameters on the malachite green removal efficiency. It has been found that 23.80 mg/g at 25°C and 88.05 mg/g at 70°C were removed. The kinetic parameters, rate constants and equilibrium adsorption capacities, were calculated and discussed for each kinetic model. The adsorption of malachite green onto apricot stones material is well described by the pseudo second-order equation. The experimental isotherm data were analyzed by different models; the adsorption follows the Langmuir model, providing a better fit of the equilibrium data. The thermodynamics parameters such as the negative free energy \( \Delta G^\circ \) (—0.191 to —4.447 kJ/mol) and positive enthalpy \( \Delta H^\circ \) (50.86 kJ/mol) indicated the spontaneous and endothermic nature of the malachite green adsorption with a chemisorption process.

Keywords
Kinetic, isotherm, adsorption, thermodynamic, apricot stone, malachite green, modeling, equilibrium

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The effluents from the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are the main sources of the aquatic pollution (Abbas and Trari, 2015). Colored wastewaters are a direct result of the production of dyes. Indeed, many dyes and their degradation products are highly toxic for living organisms particularly the malachite green (MG; Kannan and Sundaram, 2001). Therefore, the discoloration of dyes’ effluents is an important aspect for the water treatment prior to release to the aquatic environment. The dyes are not easily degradable and are difficult to remove from wastewater by the conventional techniques (Isık and Sponza, 2005). The presence of dyes in water gives rise to a chemical and biochemical oxygen demands and high-suspended solids. Considering the discharged volume and effluent combustion, the wastewater from the textile industry (Iqbal and Ashiq, 2007) is considered as one of the most polluting among all industrial sectors. Their presence, even at very low concentrations, is visible and consequently undesirable; it may dramatically affect the photosynthetic activity in the aquatic life due to the reduced light penetration. Nowadays, various physicochemical techniques have been studied to assess their applicabilities for the treatment of this type of effluents. Among the known processes, one can include the coagulation, ozonation, precipitation, flocculation, and adsorption (Abbas et al., 2019). The latter is an effective method due to its low maintenance, simple operation, and removal effectiveness (Leigen et al., 2019). Moreover, it provides an attractive alternative, especially if the adsorbent is low cost and readily available. In this respect, activated carbon is a versatile material for the adsorption process, but remains relatively expensive. Consequently, many works were concentrated on the feasibility of abundantly available substances for the synthesis of activated carbon (Qi-Xia et al., 2019). This has prompted a growing research in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products, for the water treatment. Indeed, the commercial activated carbons remain relatively expensive, and their production and regeneration cost are limiting factors. As a result, much research has focused on low-cost precursors, especially from agricultural wastes such as rubber seed coat (Rengaraj et al., 2002), olive stones (El-Sheikh et al., 2004), sawdust (Malik et al., 2007), coir pith (Namasivayam and Kavitha, 2002), bamboo (Hameed et al., 2007), and apricot stones (Abbas et al., 2016). The remarkable adsorption capacity of activated carbons is due to their well-developed porous structure and pore size distribution, as well as the surface functional groups. The adsorption efficiency depends on the pH, polarity, solubility, molecular size of adsorbate, and the presence of other ions in solution. However, the specific mechanism by which the adsorption of organic compounds takes place on active carbons is not yet fully known. Agricultural by-products exist in large amounts and about 256,890 tons of apricot stones are produced annually in Algeria (Food and Agriculture Organization of the United Nations (FAO), 2017, Table 1). In the past, these by-products were used as fuel in rural areas but now the preparation of activated carbon is considerably encouraged and apricot stone constitutes a cheap precursor for activated carbon source. Therefore, it is important to evaluate its performance as adsorbent (Abbas et al., 2014). The advantage of using an abundant and available residual biomass namely the apricot stone, as a raw material for activated carbons gives an economical interest to the technical studies. The apricot stone used in the present study was prepared by both physical and chemical activations and this study was performed with the aim to optimize the initial dye concentration, pH, grain size, contact time, adsorbent dose,
agitation speed, and temperature. In addition, the equilibrium adsorption data were fitted to different models to get constants related to the adsorption process. Equilibrium and kinetic analysis were performed to determine the parameters governing the adsorption rate, the optimization of physical parameters in the MG elimination, and the possibility of using this material as an inexpensive adsorbent for dye removal.

Experimental

Materials and methods

Analytical grade reagents were used in all experiments. MG (99%) a basic dye was purchased from Merck Company; its chemical and physical properties are listed in Table 2. Activated carbon was elaborated by carbonization and chemical activation with H$_3$PO$_4$ (85%) as follows:

**Chemical activation.** The apricot kernels from Boumerdes region (30 km east of Algiers) are air-dried, ground, and screened to obtain two fractions with average sizes ranging from 63 μm to 2.5 mm.

100 grams of the selected fraction of the precursor were impregnated in H$_3$PO$_4$ solution of purity (85%) in a mass ratio (1/2), for 24h to allow a good contact between acid and
apricot nucleus shell and to increase the pores’ diameter. The material was thoroughly washed in distilled water to remove free acid until the pH reaches 6.8 and dried at 105°C. Then, the power was introduced into a programmable muffle furnace at 250°C for a period of 4 h.

The apricot stones were mechanically ground and screened to powders of different particle sizes: <63, 63–80, 80–100, 100–200, 200–315, 315–800 µm and 0.8–1, 1–1.6, 1.6–2 mm.

The temperature, time, and phosphoric acid were selected according to the recent literature, economic cost of preparation, and environmental impact.

Characterization of activated carbon

Chemical and physical analysis of the prepared activated carbon (ASM). The Fourier transform infrared spectroscopy (FTIR) was used to identify the characteristic functional groups of ASM; 5 mg of ASM were mixed with KBr of spectroscopy quality and pressed under a pressure of 4500 lbf/in² to form thin disc. The spectra were plotted with a Perkin Elmer 2000 infrared spectrometer. The sample was scanned from 4000 to 400 cm⁻¹ for 16 times to increase the signal-to-noise ratio.

To visualize the surface structure of the prepared ASM before MG adsorption, scanning electron micrographs were taken with different resolutions thanks to a scanning electron microscope (JOEL-5910) under the following operating conditions: (Quanta, WD, HFW) 50, 9.3, 128 µm, respectively, detector: LFD, spot: 4.0, HV: 5.00 kV, magnification: 2000×.

The specific surface areas of adsorbents were measured from the N₂ adsorption–desorption isotherm using a pore size Micrometric-9320 equipment surface analyzer at the relative pressure ($P/P_o = 0.308$). The micropore volumes were evaluated with the accumulative pore volume using the t-plot method. The total pore volume was calculated from the volumes of N₂ absorbed at relative pressure ($P/P_o = 0.349$).

For the elemental analysis, the sample (~2 mg) was finely ground and placed in a microanalyzer (type LECO CHNO-932) equipped with an electronic balance and a programmable temperature regulator.

The carbon, hydrogen, and nitrogen contents were determined and the oxygen content was deduced after complete combustion of the sample. Nevertheless, for most organic and mineral compounds, carbon predominates while nitrogen is at a low level.

The chemical composition of ASM in the form of oxides was determined by X-ray fluorescence (XRF) in a Rigaku RIX-3000 equipment under the following operating conditions: stingray: $K_{Lz}$, analyzer crystal: LiF200, collimator: 150 µm, sensor: flow, Not: 0.08 degrees, $V$: 0.16 s/step, $I$: 125 mA and $V$: 60 kV.

The prepared activated carbon was characterized by physical methods (bulk density and surface area) as well as chemical and adsorption properties (point of zero charge: pHpzc).

The conductivity was measured with a conductimeter type Erwika. pHpzc of ASM was obtained by the Cerovich method using 20 mL of KNO₃ solutions (0.01 M) placed in closed conical flasks. The pH of each solution was adjusted in the range (2–14) by addition of HCl or NaOH (0.1 M). Thereafter, 0.1 g of ASM was added and the final pH was measured after 24 h under agitation; pHpzc corresponds to the intersection final pH = initial pH.

Batch mode adsorption studies. The effects of the experimental parameters namely the initial MG concentration (4.45–17.6 mg/L), pH (3–11), adsorbent dose (1–10 g/L), agitation speed (100–700 r/min), and temperature (298–343 K) on the MG elimination were studied in batch...
configuration for variable contact times (0–60 min). The stock solutions were prepared by dissolving the accurate amount of MG (99%) in distilled water, and diluted to different concentrations; pH was adjusted with HCl or NaOH (0.1 M). For the kinetic studies, ASM were contacted with 10 mL of MG solutions in Erlenmeyer flasks and placed on a rotary shaker (300 r/min); the samples were withdrawn regularly and centrifuged (3000 r/min, 10 min). The residual MG concentration in the supernatant was analyzed with a Perkin Elmer UV-visible spectrophotometer model 550S ($\lambda_{\text{max}} = 494$ nm). The amount ($q_t$) of MG ions (mg/g) adsorbed by ASM was calculated from the relation

$$q_t = \frac{(C_0 - C_t)}{m} \cdot V$$

where $C_0$ is the initial MG concentration (mg/L), $C_t$ the concentration at time ($t$), $V$ the volume of solution (L), and $m$ the ASM mass (g).

**Error analysis:** Due to the inherent bias resulting from the linearization of the isotherm models, the non-linear regression root mean square error (RMSE), the sum of error squares (SSE), and chi-squares ($X^2$) tests were used as criteria for the quality of fitting (Zahia et al., 2019a)

$$\text{RMSE} = \sqrt{\frac{1}{N-2} \sum_{i=1}^{N} (q_{e,\text{exp}} - q_{e,\text{cal}})^2}$$

$$\text{SSE} = \frac{1}{N} \sum_{n=1}^{\infty} (q_{e,\text{cal}} - q_{e,\text{exp}})^2$$

$$X^2 = \sum_{i=1}^{N} \left( \frac{q_{e,\text{exp}} - q_{e,\text{cal}}}{q_{e,\text{cal}}} \right)^2$$

where $q_{e,\text{exp}}$ (mg/g) is the experimental uptake, $q_{e,\text{cal}}$ the calculated uptake using a model (mg/g), and $N$ the number of experimental observations (the number of data points); the smaller RMSE value indicates the better fitting.

**Results and discussion**

**Characterization of the prepared ASM**

The physical and chemical properties of ASM and the elementary analysis are gathered in Table 3. Examination of the physico-chemical properties of the elaborate ASM (Figure 1) shows that the chemical and physical activation has developed a porosity and increased the specific surface area up to 80.05 m$^2$/g for the fixing the maximum pollutant. The elemental analysis shows the predominance of the percentage of carbon (48.45%); in correlation with the adsorbents reported in the literature. The analysis by laser heating shows that the precursor used has a low moisture content (1.48%), the percentage of organic matter determined by XRF is found to be 98.32%.
Structural characterization by infrared spectroscopy

The FTIR spectra of the adsorbent (Figure 2) show many absorption peaks, characteristic of functional groups of the adsorbent (Abbas et al., 2018). The large band in the region (3122–3680 cm$^{-1}$) is due to –OH groups (unrelated –OH function and intermolecular hydrogen band). The bands centered at 2929 and 1508 cm$^{-1}$ suggest the presence of –CH$_2$ groups (symmetric and antisymmetric) while the band in the region (1600–1665 cm$^{-1}$) indicates the presence of C–H, –C=C– and C=C groups. The peak at 1732 cm$^{-1}$ is assigned to C=O bond in the carboxylic groups. Such results clearly show that the functional groups including carboxylic and hydroxyl groups contribute to the MG adsorption.

To explain the adsorption process that took place between the pollutant and the adsorbent charged with the opposite sign, attractive electrostatic forces are exerted between the charges for fixing in the surface sites which gradually decrease over the dye occupation. Once the saturation is reached, the pollutant enters the deepest sites under the effect of the
gradient concentrations; the general mechanism can be summarized by the following sequence of reactions:

- Transfer of the pollutant from the outer to inner layer (very fast step).
- Displacement of the pollutant until it comes into contact with the adsorbent (rapid step).
- Diffusion of the pollutant into the adsorbent under a concentration gradient (slow step).
- Adsorption of the pollutant in the micropores (very fast step).

**Adsorption mechanism**

The adsorption mechanism can be explained as a function of the interactions of functional groups of the adsorbent with the dye. For this, the second-order kinetic model is in perfect correlation with the experimental results. Intraparticle diffusion does not dominate the mechanism but contributes to the adsorption process. The free energy and enthalpy change during the adsorption of MG on ASM, suggesting that chemisorption (the formation of new chemical bonds), are the main mechanisms controlling the adsorption process. According to Iqbal and Ashiq (2007), the presence of larger pores promotes higher adsorption capacities, particularly for dyes. The surface chemistry is another important factor that controls the adsorption. Highly functionalized surfaces with carboxylate and ketone groups can readily chemisorb cationic dyes. The carbonaceous material has the potential to absorb the MG; the considerable number of oxygen-containing functional groups on the surface of the carbonized adsorbent provides adequate adsorption sites and increases the adsorption capacity of the pollutant. The adsorption mechanisms are mainly due to the formation of hydrogen bonds, hydrophobic interactions, and electrostatic forces of the pollutants with the activated carbon.
The main binding sites of MG by activated carbons are the hydroxyl and carboxyl groups on the surface of the ASM adsorbent that react with polar molecules and various functional groups. The surface of the porous activated carbon may include electrically charged groups (pHzpc). The isoelectric pH of ASM determined by the Cerovich method is 7.05, this is explained by: a predominance of negative adsorbent charges for above 7.05, favorable for the fixation of MG, a cationic dye, because the electrostatic forces are attractive for the formation of new bonds, which is correlated with the results obtained according to the thermodynamic study (chemisorption process). A predominance of the adsorbent positive charges below pH 7.05 makes the attraction of the MG pollutant overcome, since there is repulsion between the positive charges of the pollutant and the positive charges of the adsorbent. This phenomenon causes a low dye adsorption (only by force of hydrogen bonds of London, Kessan). This observation was reworked during the study of the pH effect of pH on the adsorbed quantity of MG (pH < 7.05).

**Effect of analytical parameters**

In the first stage of batch MG adsorption onto ASM, the effect of grain sizes is examined. Significant variations in the elimination capacity and removal efficiency were observed from 63 μm to 2 mm, showing that the best performance occurs in the range (800 μm to 2 mm). If we examine the effect of granulometry (Figure 3), we notice that for small dimensions 63–80, 80–100, 100–200, 200–315, and 315–800 μm the adsorbed quantity gradually increases from

![Figure 3](image-url)  
**Figure 3.** Effect of particle size on the MG adsorption efficiency (T: 25°C, C₀: 10 mg/L, V: 10 mL, contact time: 40 min, stirring speed: 400 r/min, adsorbent dosage: 1 g/L and pH: 10).
3.5 to 7.3 mg/g. The adsorption is maximal in the region (800 \mu m–2 mm) which is explained by the saturation of the adsorbent pores for a quantity of 7.5 mg/g. Moreover, this phenomenon can be interpreted by the presence of large adsorbent particles with the presence of larger surface pores (longer and deeper pore length). The electrostatic attraction of the pollutant by the adsorbent sites is favorable, allowing an increase in the uptake dye quantity. The size in the range of 800 \mu m–2 mm is consequently used in all adsorption experiments.

The pH is a crucial parameter in adsorption and the percentage of MG removal increases consistently with decreasing pH (Figure 4). The pH effect on the MG adsorption by ASM can be explained on the basis of pHpzc, for which the charge of the adsorbent surface is positive below pHpzc of (ASM = 7.05). As the pH decreases, the number of positively charged sites augments and improves the MG adsorption by electrostatic attractions. Similar experimental details have been reported (Abbas et al., 2018).

Figure 5 presents the influence of the stirring speed on the MG adsorption on ASM. The maximum uptake was obtained for variable speeds (400–450 r/min). Such moderate speed gives a good homogeneity for the mixture suspension and precludes the vortex phenomenon.

The adsorption capacity of MG increases over time to reach a maximum after 40 min and thereafter tends to saturation, indicating that no more MG molecules are further removed from the solution. The initial MG concentration from 4.45 to 17.6 mg/L yields an increased adsorbed amount from 3.60 to 8.20 mg/g (Figure 6). This is ascribed to the increased driving force which comes from the concentrations gradient which overcomes the mass transfer resistance of MG ions between the liquid and solid phases.

For the first stage of batch adsorption onto ASM and the influence of adsorbent dose is examined. Significant variations in the uptake capacity and removal efficiency for various
Figure 5. Effect of stirring speed on the MG dye adsorption capacity (T: 25°C, C₀: 10 mg/L, pH: 10, absorbent dosage: 1 g/L, particle size: 800–2000 μm).

Figure 6. Effect of the contact time on the adsorption of MG onto ASM for different initial concentrations (T: 25°C, pH: 10, stirring speed: 400 r/min, absorbent dosage: 1 g/L, and particle size: 800–2000 μm).
Adsorbent doses (1–10 g/L) indicate that the best performance is obtained for a dose of 1 g/L (Figure 7). This result was expected because the removal efficiency generally increases by the fact that more mass available, more the contact surface offered to the adsorption. Moreover, higher adsorbent dose in solution leads greater availability of exchangeable sites for the ions. The decrease in the dye adsorption with the increase of the adsorbent dose is due to a large amount of adsorption sites on the surface of the adsorbent, which implies that a large amount of adsorbate is required to saturate the adsorbent.

**Adsorption isotherms**

The shape of the isotherms is an experimental tool to diagnose the type of the adsorption. They are classified in four groups namely L, S, H, and C (Giles et al., 1960), and ASM at (25°C and 70°C) displays L type (Figure 8). The initial part of the L curve indicates a small interaction between the basic dye MG and the carriers at low concentrations. However, as the MG concentration in the liquid phase increases, the adsorption occurs more readily. This behavior is due to a synergistic effect, with the adsorbed MG molecules facilitating the adsorption of additional molecules as a result of attractive interaction adsorbate–adsorbate. The equilibrium isotherm model is used to describe the adsorption data; the underlying thermodynamic parameters of these models provide insights for the adsorption mechanism, surface properties, and affinity of the adsorbent. The importance of obtaining the best isotherm becomes more significant, because as more applications are developed, more accurate and detailed isotherm descriptions are required for the adsorption system designs.

**Figure 7.** Effect of adsorption dose on the MG dye adsorption capacity (T: 25°C, C₀: 10 mg/L, pH: 8, stirring speed: 400 r/min, contact time: 40 min and particle size: 800–2000 μm).
The Langmuir model (Gerente et al., 2007) is the best known and most widely applied, it is represented by the linear form

\[ \frac{1}{q_e} = \frac{1}{q_{\text{max}}} - \frac{1}{q_{\text{max}} \cdot K_L \cdot C_e} \]  

(5)

where \( C_e \) is the equilibrium concentration (mg/L), \( q_{\text{max}} \) the monolayer adsorption capacity (mg/g), and \( K_L \) the constant related to the free adsorption energy (L/mg), determined from the plot \( (1/q_e) \) versus \( (1/C_e) \). The applicability to the adsorption is compared by evaluating the statistic RMSE values at 25°C. The smaller RMSE values obtained for the models indicate a better fitting. The essential features of the Langmuir isotherm (Figure 9(a) and (b)) can be expressed in terms of dimensionless separation factor \( R_L \) (Zahia et al., 2019a).

The Freundlich isotherm (Freundlich, 1906) is valid for non ideal adsorption on heterogeneous surfaces as well as multilayer sorption

\[ \ln q_e = \ln K_F + \frac{1}{n} \cdot \ln C_e \]  

(6)
The constant $K_F$ characterizes the adsorption capacity of the adsorbent (mg$^{1-1/n}$ L$^{1/n}$ g$^{-1}$) while $n$ is an empirical constant related to the magnitude of the adsorption driving force. Therefore, the plot ln $q_e$ versus ln $C_e$ permits the determination of both the constant $K_F$ and $n$.

The Temkin isotherm describes the behavior of adsorption systems on heterogeneous surfaces, and is applied in the following form (Temkin and Pyzhev, 1940)

$$q_e = \frac{RT}{b} \cdot \ln AC_e = B\ln A + B\ln C_e$$ (7)

The adsorption data are analyzed according to equation (7). Therefore, the plot $q_e$ versus ln $C_e$ leads to determine the constants $A$ and $B$.

The Elovich isotherm (Ozcan et al., 2006) is based on the principle of the kinetic, assuming that the number of adsorption sites augments exponentially with the adsorption, implying a multilayer adsorption described by

$$\ln \frac{q_e}{C_e} = \ln (q_{\text{max}}, K_E) - \frac{q_e}{q_{\text{max}}}$$ (8)

where $K_E$ (L/mg) is the Elovich constant at equilibrium, $q_{\text{max}}$ (mg/g) the maximum adsorption capacity, $q_e$ (mg/g) the adsorption capacity at equilibrium, and $C_e$ (g/L) the concentration of the adsorbate at equilibrium. Both $K_E$ and $q_{\text{max}}$ are calculated from the plot of ln ($q_e/C_e$) versus $q_e$.

The Redlich-Peterson equation (Limousin et al., 2007). This three-parameter mono soluted model is one of the most used in the literature because it is advertised as applicable over a wide range of concentrations. It is an empirical model combining the parameters of the Langmuir and Freundlich equations and its equation is as follows

$$q_e \frac{q_{\text{max}}}{K_1} = \frac{K_1 C_e}{1 + (K_1 C_e)^n}$$ (9)

The theoretical parameters along with the determination coefficients RMSE, SSE, and $X^2$ are listed in Table 4. One can see that the Langmuir isotherm model exhibits the higher RMSE, $X^2$, and SSE values.

Adsorption kinetics

The kinetic study is important in the adsorption, it describes the uptake rate of adsorbate and controls the residual time of the whole process. The pseudo first-order and pseudo second-order (Figures 10 and 11) are selected in this study to describe the adsorption.

The pseudo first-order equation (Lagergren, 1998) is given by

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \cdot t$$ (10)

The pseudo second-order model (Ho and Mc Kay, 2000) is expressed by

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t$$ (11)
where $q_t$ (mg/g) is the amount of MG adsorbed at various times $t$ (min), $K_1$ the rate constant (min$^{-1}$) and $K_2$ the rate constant of the pseudo-second order kinetic (g/mg.min). For the pseudo-first order kinetic, the experimental data deviate from linearity as evidenced by the low $q_e$ values and coefficients and is therefore inapplicable for the present system.

### Table 4. Sorption isotherm coefficients of different models.

| Model                  | Parameters | $T = 25\degree$C | $T = 70\degree$C |
|------------------------|------------|-------------------|-------------------|
| **Langmuir ($I$)**     | $1/Q_e = f (1/C_e)$ | $Q_{max}$: 23.80 mg/g | $Q_{max}$: 83.33 mg/g |
|                        |            | $K_I$: 0.314 L/mg  | $K_I$: 0.0085 g/mg |
|                        |            | $R^2$: 0.999      | $R^2$: 0.999      |
|                        |            | $X^2$: 0.188      | $X^2$: 0.208      |
|                        |            | SSE: 0.35         | SSE: 0.39         |
|                        |            | RMSE: 0.59        | RMSE: 0.72        |
| **Langmuir ($V$)**     | $1/C_e = f (1/Q_e)$ | $Q_{max}$: 23.94 mg/g | $Q_{max}$: 88.5 mg/g |
|                        |            | $K_I$: 0.312 L/mg  | $K_I$: 0.0088 g/mg |
|                        |            | $R^2$: 0.999      | $R^2$: 0.999      |
|                        |            | $X^2$: 0.185      | $X^2$: 0.207      |
|                        |            | SSE: 0.37         | SSE: 0.38         |
|                        |            | RMSE: 0.61        | RMSE: 0.68        |
| **Freundlich**         | $\ln Q_e = f (\ln C_e)$ | $K_F$: 2.199 (mg$^{-1/1}/L^{-1/1}$g$^{-1}$) | $K_F$: 0.922 mg/g |
|                        |            | $1/n$: 1.917      | $1/n$: 0.845      |
|                        |            | $R^2$: 0.989      | $R^2$: 0.996      |
|                        |            | $X^2$: 212.33     | $X^2$: 256.33     |
|                        |            | SSE: 14787.9      | SSE: 15678.9      |
|                        |            | RMSE: 121.61      | RMSE: 128.61      |
| **Elovich**            | $\ln (Q_e/C_e) = f (q_e)$ | $Q_{max}$: 8.62 mg/g | $Q_{max}$: 142.8 mg/g |
|                        |            | $K_L$: 1.198 g/mg  | $K_L$: 0.0088 g/mg |
|                        |            | $R^2$: 0.984      | $R^2$: 0.89       |
|                        |            | $X^2$: 0.064      | $X^2$: 0.123      |
|                        |            | SSE: 0.092        | SSE: 0.1025       |
|                        |            | RMSE: 0.303       | RMSE: 1.36        |
| **Temkin**             | $Q_e = f (\ln C_e)$ | $K_T$: 3.904 L/mg  | $K_T$: 0.2028 L/mg |
|                        |            | $\beta_T$: 4.37   | $\beta_T$: 10.028 |
|                        |            | $\Delta Q$: 13.556 kJ/mol | $\Delta Q$: 25.167 kJ/mol |
|                        |            | $\beta_T': RTQ_m/\Delta Q$ | $\beta_T': RTQ_m/\Delta Q$ |
|                        |            | $R^2$: 0.987      | $R^2$: 0.948      |
|                        |            | $X^2$: 0.055      | $X^2$: 0.066      |
|                        |            | SSE: 0.036        | SSE: 0.055        |
|                        |            | RMSE: 0.189       | RMSE: 2.189       |
| **Redlich-Peterson**   | $C_e/Q_e = f (C_e^n)$ | $K$: $-3.904$ g/L | $K$: $8.888$ mg/g |
|                        |            | $Q_m$: 8.88 mg/g   | $Q_m$: 0.993      |
|                        |            | $R^2$: 0.993      | $R^2$: 1.236      |
|                        |            | $X^2$: 1.236      | SSE: 10.236       |
|                        |            | RMSE: 7.125       | RMSE: 2.189       |

RMSE: root mean square error; SSE: sum of error squares.
Figure 10. Pseudo first-order kinetic for the adsorption of MG onto ASM (pH: 10, 800–2000 μm particle size, 1 g/L adsorbent dosage, 400 r/min stirring speed, temperature 25°C, and contact time: 40 min).

Figure 11. Pseudo-second order kinetic for the adsorption of MG onto ASM (pH: 8, 800–2000 μm particle size, 1 g/L adsorbent dosage, 400 r/min stirring speed, temperature 25°C, and contact time: 40 min).
On the contrary, the determination coefficient and $q_{\text{cal}}$ of the pseudo-second order kinetic model agree with the experiments (Table 5).

**Elovich equation** (Gerente et al., 2007). Although the Elovich equation was firstly used in the kinetics of chemisorptions of gases on solid, it has been successfully applied for the adsorption of solutes from a liquid solution. The Elovich equation is given as follows

$$q_t = \frac{1}{\beta} \ln \alpha + \frac{1}{\beta} \ln t$$

(12)

where $\alpha$ (mg/g min) is the initial sorption rate, the parameter $\beta$ (g/mg) is related to the extent of surface coverage and activation energy for the chemisorptions. The plot $q_t$ versus ln $t$ was used to determine the constants $\alpha$ and $\beta$.

**Effect of temperature**

Figure 12 clearly shows that the adsorption capacity of ASM increases with increasing the MG concentration (10 to 20 mg/L) and temperature (295 to 323 K), indicating that the adsorption is favored at high temperature. The free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$) are determined by the following equations (Kin et al., 2005; Zahia et al., 2019b)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

(13)

The free energy is composed of the enthalpic term ($\Delta H^\circ$) which expresses the energies of interactions molecules/adsorbent surface, and entropic term ($\Delta S^\circ$) which expresses the modification and arrangement of the molecules in the liquid phase and on the surface.

The thermodynamic behavior for MG adsorption onto ASM was further investigated. The thermodynamic parameters $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ are calculated from the relation
\[ \Delta G^\circ = -RT \ln K_o \] (14)

\( K_o \) is the apparent equilibrium constant. \( \Delta H^\circ \) and \( \Delta S^\circ \) are calculated from the adsorption data at different temperatures using the relation

\[ \ln K_o = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \] (15)

The values of \( \ln K_o \) were obtained from equilibrium constant \( (K_s) \)

\[ K_s = \frac{q_e}{C_e} \times \frac{\gamma_1}{\gamma_2} \] (16)

where \( \gamma_1 \) is the activity coefficient of the adsorbed solute and \( \gamma_2 \) the activity coefficient of the solute in the equilibrium suspension. The ratio of activity coefficients was assumed to be uniform for dilute solutions. As the MG concentrations in solution approached zero, the activity coefficient approached unity

\[ \lim_{C_e \to 0} \frac{q_e}{C_e} = K_0 \] (17)

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**Figure 12.** Temperature effect on the adsorption of MG onto ASM \((C_o: 10 \text{ to } 20 \text{ mg/L}, \text{pH: } 10, \text{adsorbent dosage: } 1 \text{ g/L, particle size: } 800\text{--}2000 \mu \text{m, stirring speed: } 400 \text{ r/min and contact time: } 40 \text{ min}). \)
The values of $K_0$ determined from intercept (figures not shown), by plotting $\ln(\frac{q_e}{C_e})$ versus $C_e$ and extrapolating to $C_e = 0$ at different temperatures (Ghaedi et al., 2013). $\Delta H^0$ and $\Delta S^0$ obtained from the slope and intercept of the plot $\ln K$ versus $1/T$ (Figure 13) and $\Delta G^0$ at various temperatures are summarized in Table 6. The negative free energy $\Delta G^0$ ($-0.191$ to $-4.447$ kJ/mol) and positive enthalpy $\Delta H^0$ ($50.86$ kJ/mol) indicate that the adsorption of MG onto ASM is spontaneous and endothermic. The positive entropy $\Delta S^0$ ($171$ J/mol.K) states clearly that the randomness increases at the solid–solution interface during the MG adsorption, indicating that some structural exchange occurred among the active sites of the adsorbent and MG.

**Performance of the prepared ASM**

In order to evaluate the efficiency of ASM, a comparison of basic dye adsorption of this work is made with other relevant studies (Table 7) and the adsorption capacity ($q_{max}$) is the key comparative parameter. We can see that our $q_{max}$ value is in good agreement with most
previous works, suggesting that MG could be easily adsorbed on ASM prepared in the present work and the apricot stones, very abundant in Algeria, are effective adsorbent for the MG adsorption. ASM is a promising adsorbent for heavy metals and basic dyes owing to pHpzc, and our perspective in the future is to achieve the adsorption tests in column mode using industrial effluents. Such results are currently under way and will be reported in a next future.

**Conclusion**

This study has shown that the activated carbon prepared from apricot stone can be employed as effective adsorbent for the removal of MG in aqueous solution. The Langmuir model provided a better fit of the equilibrium adsorption data. It gave a maximum adsorption capacity of 23.80 mg/g at 25°C which increased down to 88.05 mg/g at 70°C at pH 10.

| Adsorbants                  | $q_{\text{max}}$ (mg/g) | $T$ (°C) | pH | $t_{\text{eq}}$ (h) | References                  |
|-----------------------------|--------------------------|-----------|----|---------------------|-----------------------------|
| Activated carbon            | 565                      | 32        | 10 | 48                  | Kumar (2006)                |
| Jute fiber carbon           | 136.6                    | 25        | 10 | 6                   | Porkodi and Kumar (2007)    |
| Biomass of phitophora       | 117.6                    | 30        | 5  | 8                   | Kumar et al. (2005)         |
| Activated carbon (waste apricot) | 116.3                | 30        | 9  | 1                   | Basa (2006)                 |
|                             | 158.73                   | 40        | 8  | 1                   |                             |
|                             | 163.93                   | 50        | 8  | 1                   |                             |
| Cyclodextrin-based adsorbent| 91.9                     | 25        | 8  | 2                   | Crini et al. (2007)         |
| Hen feathers                | 10.29                    | 25        | 5  | 3                   | Mittal (2006)               |
|                             | 10.69                    | 40        | 5  | 3                   |                             |
|                             | 35.79                    | 50        | 5  | 3                   |                             |
| Arundo Domax root carbon    | 8.49                     | 20        | 5  | 3                   | Zhang et al. (2008)         |
|                             | 8.69                     | 30        | 5  | 3                   |                             |
|                             | 9.35                     | 40        | 5  | 3                   |                             |
| Sugar cane dust             | 4.88                     | 25        | 7.5| 0.5                 | Khattri and Singh (1999)    |
|                             | 4.57                     | 35        | 7.5| 0.5                 |                             |
|                             | 4.08                     | 45        | 7.5| 0.5                 |                             |
| Lemon peel                  | 51.73                    | 32        | 10 | 25                  | Kumar and Sivanesan (2007)  |
| Caulerpa racemosavar cylindracea | 19.88               | 25        | 6  | 1.5                 | Bekci et al. (2009)         |
|                             | 21.74                    | 25        | 6  | 1.5                 |                             |
|                             | 25.67                    | 25        | 6  | 1.5                 |                             |
| Bamboo-based activated carbon| 263.6                  | 30        | 8  | 3.5                 | Hameed and El Khaiary (2008) |
| Commercial activated carbon | 8.27                    | 30        | 7  | 3                   | Mall et al. (2005)          |
| Laboratory grade            | 42.18                    | 30        | 7  | 3                   |                             |
| Bagasse fly ash             | 170                      | 30        | 7  | 3                   |                             |
| Rubber wood sawdust         | 36.3                     | 30        | 9  | 48                  | Kumar and Sivanesan (2007)  |
| Functionalized sawdust      | 85.47                    | 25        | 8  | 25                  | Renmin et al. (2009)        |
| Crude sawdust               | 196.08                   | 25        | 8  | 25                  |                             |
| Dead tree leaves            | 78.45                    | 25        | 9  | 0.5                 | Oualid et al. (2008)        |
|                             | 83.21                    | 35        | 9  | 0.5                 |                             |
|                             | 86.21                    | 45        | 9  | 0.5                 |                             |
| Apricot stone activated carbon (ASM) | 23.94                | 25        | 10 | 40 min              | This study                  |
| ASM                         | 88.5                     | 70        | 10 | 40 min              |                             |
The pseudo second-order model proved the best description of the kinetic data. The negative free energy $\Delta G^\circ$ and positive enthalpy $\Delta H^\circ$ indicate that the adsorption of MG onto ASM is spontaneous and endothermic over the studied temperatures range. The positive entropy $\Delta S^\circ$ states clearly that the randomness increases at the solid–solution interface during the MG adsorption onto ASM, indicating that some structural exchange occurred among the active sites of the adsorbent and MG ions.

The MG adsorption follows a pseudo second-order kinetic model, which relies on the assumption that the chemisorptions may be the rate-limiting step. The MG molecules are attached to the adsorbent surface by forming a chemical bond and tend to find sites that maximize their coordination number with the surface. The kinetic and thermodynamic data can be further explored for the design of absorber for industrial effluents treatment.

The results of the present investigation showed that ASM is a potentially useful adsorbent for the MG adsorption, an issue of environmental concern and the natural abundance of this food waste can provide an adsorption medium which contributes to the wastewater treatment. The comparison of the adsorption capacity of the prepared adsorbent with other adsorbents shows its attractive properties from industrial and economic interests.

This study in tiny batch gave rise to encouraging results, and we wish to achieve the adsorption tests in column mode under the real conditions applicable to the treatment of industrial effluents and to test the homogeneous photodegradation of MG on TiO$_2$ and SnO$_2$ semiconductors is the future objective of this work.

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