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Valorisation of *Balanites aegyptiaca* shells through the production of activated Carbon application to the removal of methylene blue (MB) in aqueous solution

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Abstract: The objective of this study is to develop activated carbon from *Balanites aegyptiaca* shells and test its effectiveness in treating wastewater containing dyes such as methylene blue. The results of the physicochemical characterisation has showed that the activated carbon developed has good adsorbent properties, as demonstrated by the methylene blue and iodine indices. The performance evaluation of the developed carbon shows that the optimal conditions for Methylene Blue (MB) adsorption on activated carbon correspond to a carbon weight of 0.5 g, an initial MB concentration of 100 mg.L^{-1}, a contact time of 60 min and a temperature of 30°C. The kinetic study shows that adsorption follows a pseudo-second-order model. Isotherm modelling also has showed that the Langmuir model is the most suitable has model to describe the fixation of methylene blue on carbon. The thermodynamic study showed that the fixation of methylene blue is a spontaneous and exothermic process. In summary, the results of this study confirm that *Balanites aegyptiaca* shells can be used to produce activated carbon that is effective for treating industrial effluents containing dyes.

1. Introduction

Nowadays, with population growth and continuous industrial development, industrial and urban waste contributes significantly to environmental pollution (Ahsaine *et al.,* 2018). The textile industry is one of the largest sources of pollution (Khan *et al.*, 2020; Saratale *et al.*, 2020; N'diaye *et al.*, 2022). It generates significant quantities of wastewater containing several types of dyes. In fact, 10 to 15% of global dye production, estimated at between 800,000 and 1 million tonnes, is discharged into the environment each year (Machrouhi *et al.,* 2019; Mehr *et al.,* 2020). That is the reason why wastewater treatment is becoming essential for the protection of humans and the environment. Several techniques have been developed to treat this wastewater (Ani *et al.,* 2020; Kato & Kansha, 2024; Soliman & Moustafa, 2020). Adsorption on activated carbon stays one of the most widely used techniques due to its effectiveness. That is why new sources of precursor materials that are unconventional, renewable, available, and inexpensive are being explored. Several studies have focused on the development of activated carbons based on lignocellulosic biomass such as agricultural residues and forestry waste: wood wax (Jiang *et al.*, 2021), coconut shells (Pino *et al.,* 2006), jatropha shells (Jain *et al.,* 2015), baobab shells (Ndiaye *et al.,* 2022; Nedjai *et al.,* 2021), peanut shells (Georgin *et al.*, 2016), rice husks (Ahmaruzzaman & Gupta, 2011), orange peels (Akinhanmi *et al.*, 2020), banana peels (Moubarak *et al.*, 2014), potato peels (Enenebeaku *et al.,* 2017), etc.

In Senegal, *Balanites aegyptiaca* is one of the most widespread plants (Diedhiou, 2017; Ndong *et al.,* 2015). Balanites fruits are widely consumed due to their many therapeutic properties (Dekkar and Kalaidji; Diedhiou, 2017). The seeds are crushed to obtain a highly prized oil, but this process generates significant quantities of by-products. The oil has several applications, including food, cosmetics, and fuel (Adamou *et al.*, 2020; Chapagain *et al.,* 2009; Zang *et al.*, 2018). However, the balanites shells, which are considered waste, could be of great interest in the production of activated carbon.

The goal of this study is to recover value from *Balanites aegyptiaca* shells, a lignocellulosic waste product, by developing activated carbon which is effective for wastewater treatment. This will involve, on the one hand, developing activated carbon from Balanites seed shells using chemical processes and determining its physicochemical parameters and, on the other hand, evaluating the performance of the carbon developed for the removal of Methylene Blue (MB) in aqueous solution. To this end, the influences of operating parameters such as the adsorbent dose, adsorption time, initial MB concentration in the solution, initial pH of the solution and reaction medium temperature will be evaluated. The kinetics and adsorption isotherms of MB on activated carbon will also be modelled.

2. Methodology

2.1. Production of activated carbon

2.1.1. Pre-treatment of raw materials

The raw material used in this study consists of *Balanites aegyptiaca* fruits (**Figure 1**) collected at the Sandaga market in Dakar region (Senegal). The fruits are first soaked in water for 24 hours to ease pulping. After pulping, the seeds are dried in an oven at 105°C for 24 hours and then crushed to separate the shell from the kernel. The shells are ground using an electric grinder and then sieved to obtain a powder with a particle size of less than 800 µm, which is used to produce activated carbon.

Figure 1. Raw material

2.1.2. Preparation of activated carbons

Activated carbon is produced from B. aegyptiaca seed shell powder, previously obtained, by chemical means using phosphoric acid (H_3PO_4, 85%) as an activating agent. The production process adopted is based on the work of DIOP et al. (Diop et al., 2022). Balanites seed shell powders with a particle size of less than 800 µm are mixed with the activating agent solution at an impregnation ratio (precursor mass/acid solution agent mass) of 1/3. The mixture is then stirred for 1 hour at room temperature (approximately 25°C) to ensure good diffusion of the activating agent within the material, then placed in an oven at 120°C for 6 hours. After impregnation, the particles are directly pyrolysed at 528°C for 1 hour in the oven. The charcoal obtained in this way is cooled in a desiccator and then washed with distilled water to remove traces of acid and other impurities until the wash water is pH neutral, before being dried in an oven at 105°C for 24 hours.

2.2. Preparation of the adsorbate

In this study, Methylene Blue (MB), methylthioninium chloride, was used as a dye. The dye stock solution was used prepared by dissolving 1 g of dye in 1 L of distilled water, and the solutions with the desired dye concentrations were then developped then prepared by diluting the stock solution. Hydrochloric acid and sodium hydroxide solutions were used to adjust the pH of the solutions.

2.3. Determination of the physical and chemical parameters of different activated carbons

2.3.1. Determination of pH

The pH is found according to ASTM method 3838-80. Approximately 1 g of charcoal is placed in an Erlenmeyer flask and 100 mL of distilled water is then added. The mixture is stirred for 1 hour and then filtered. The pH of the filtrate is measured using a pH meter (HI 2211, Hanna Instruments, France).

2.3.2. Determination of moisture content

Moisture content is determined following standard NF V 03-603 by measuring the loss in weight of a sample weighing approximately 1 g that has been dried in an oven at 105°C until a constant mass is obtained.

2.3.3. Determination of ash content

The mineral matter (MM) or ash content is determined by the loss in weight, based on the dry matter, by calcination of the latter in an electric muffle furnace at approximately 550°C for three hours (NF V 03-922). The sample is then cooled in a desiccator and weighed.

2.3.4. Determination of bulk density

To determine the bulk density, a 50 mL flask is filled to the mark with the material. The bulk density is calculated from the mass of the sample and the apparent volume of the sample.

2.3.5. Determination of iodine index

The iodine molecule was chosen as the reference molecule to evaluate the adsorption capacity of small molecular solutes < 10 Å (Kouotou et al., 2013). The iodine index is determined according to the AWWA B 600 – 78 methods (Gueye, 2015). It is defined as the quantity, in milligrams of iodine, adsorbed by 1 g of adsorbent. A known mass of carbon, previously dried at 105°C for 24 hours, is brought into contact with a known volume of iodine solution of known concentration. The mixture is stirred for 30 minutes before being filtered. The filtrate is titrated with a sodium thiosulphate solution using starch as a color indicator. The amount of iodine adsorbed is then determined using the following formula:

$$I_I = \frac{(C_i - C_f) \times V}{w_{CA}} \quad \textbf{Eqn. 1}$$

I_I being the iodine index in $mg.g^{-1}$; C_i, the initial weight concentration of iodine in $mg.L^{-1}$; C_f, the final weight concentration of iodine in $mg.L^{-1}$; V, the volume of the adsorbed iodine solution in L; and w_{AC}, the weight of adsorbent in g.

2.3.5. Determination of methylene blue index

Methylene blue was chosen as the reference molecule for evaluating the adsorption capacity of solutes larger than 15 Å (*Kouotou et al., 2013*). In other words, the methylene blue index is considered as the basis to measure the adsorption capacity of large and medium-sized molecules. It represents the quantity, in milligrams of methylene blue, adsorbed by 1 g of adsorbent. The method used to determine it is based on the work of DAS (Das, 2014). Approximately 1 g of pre-dried carbon is placed in contact with 50 mL of a 200 $mg.L^{-1}$ methylene blue solution for 30 minutes under continuous stirring. After adsorption, the residual concentration of methylene blue is measured using a UV spectrophotometer (Agilent Technologies Cary 60 UV-Vis) at a wavelength (λ= 654 nm). The methylene blue index is calculated by using the following formula:

$$I_{MB} = \frac{(C_i - C_f)V}{w_{AC}} \times 100 \quad \textbf{Eqn. 2}$$

I_{BM} being the methylene blue index in $mg.g^{-1}$, C_i the initial weight concentration of methylene blue in $mg.L^{-1}$, C_f the final weight concentration of methylene blue in $mg.L^{-1}$, V the volume of the adsorbed methylene blue solution in L, w_{AC} the weight of adsorbent in g.

2.4. Adsorption of methylene blue

2.4.1. Adsorption test

The adsorption tests were carried out in a batch reactor, stirred in 250 mL Erlenmeyer flasks at a stirring speed of 400 rpm. The effects of contact time, adsorbent weight, initial methylene blue concentration, temperature and pH were studied. After each adsorption test, the solutions are filtered through filter paper and the filtrates are analyzed to determine the residual concentration of methylene blue by using a spectrophotometer (UV-Vis 60 Cary 60 Agilent Technologies). The adsorption capacity and removal rate were calculated respectively, according to **Eqn. 3** and **Eqn. 4** below:

$$Q_e = \frac{(C_i - C_f)V}{m_{CA}} \times 100 \quad \textbf{Eqn. 3}$$

$$\mathrm{T} = \frac{(C_i - C_f)}{C_i} \times 100 \quad \textbf{Eqn. 4}$$

Where Q_e is the adsorption capacity in $mg.g^{-1}$, C_i is the initial weight concentration of MB in $mg.L^{-1}$, C_f is the weight concentration of the solution after adsorption in $mg.L^{-1}$, V is the volume of the solution in L, and T is the MB removal rate in %.

2.4.2. Optimisation of adsorption of methylene blue on activated carbon

2.4.2.1. Influence of contact time on methylene blue removal

To determine the contact time required to reach adsorption equilibrium, the adsorption kinetics were studied by monitoring the evolution of the adsorption capacity as a function of contact time. The variation in contact time was carried out under the following conditions: initial MB concentration set at 50 mg.L^{-1}, solution volume at 100 mL, adsorbent weight at 0.3 g, temperature at 25°C and without adjusting the pH of the initial MB ready solution.

2.4.2.2. Influence of adsorbent mass on methylene blue removal

The effect of adsorbent weight on methylene blue removal was studied by varying it from 0.1 to 0.6 g. The adsorbent weight was put in contact with 100 mL of MB solution with an initial concentration of 50 mg.L^{-1} without adjusting the pH of the starting solution in 250 mL Erlenmeyer flasks. The mixture was stirred for 45 min at a temperature of 25°C. The suspensions were then filtered, and the filtrates analysed.

2.4.2.3. Influence of initial MB concentration on adsorption

To determine the maximum adsorption capacity of methylene blue, we have monitored the amount of methylene blue adsorbed as a function of the initial methylene blue concentration between 10 and 100 mg.L^{-1}. The mass of adsorbent was set at 0.5 g, the contact time at 45 min, the temperature at 25°C, and no adjustment was made to the pH of the MB solution.

2.4.2.4. Influence of temperature on the removal of methylene blue

We have studied the effect of medium temperature on the amount of MB adsorbed in a temperature range varying between 25 and 60°C, setting the solution volume at 100 mL, the initial MB concentration at 100 mg.L^{-1}, the adsorbent weight at 0.5 g and the contact time at 45 min.

2.4.2.5. Influence of pH on methylene blue removal

To determine the optimal pH for the MB adsorption process, the change in the amount of MB adsorbed was studied by varying the pH of the reaction medium from 2 to 12. To do this, the volume of the solution was set at 100 mL, the initial concentration at 100 mg.L^{-1}, the mass of adsorbent at 0.5 g, the contact time at 45 min and the temperature at 25°C.

2.4.3. Modeling of adsorption kinetic

To determine the equilibrium adsorption capacity and the adsorption mechanism, we have studied the adsorption kinetics. Four models were tested as follows:

2.4.3.1. First-order pseudo model : Lagergren model **(***Gueye, 2015***)**

$$\frac{1}{Q_t} = \frac{1}{Q_e} + \frac{K_1}{Q_e}\frac{1}{\mathrm{t}} \qquad \textbf{Eqn. 5}$$

Q_t being the adsorption capacity at time t in mg.g^{-1}, K_1 the pseudo-first-order rate constant in min^{-1}; t is the contact time in min, Q_e is the equilibrium adsorption capacity in mg.g^{-1}.

The curve $\frac{1}{Q_t}$ as a function of $\frac{1}{\mathrm{t}}$ gives a straight line with a slope equal to $\frac{1}{Q_e}$.

2.4.3.2. Second-order pseudo model : HO and McKay model (Omokpariola, 2021)

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e 2} + \frac{1}{Q_e}t \qquad \textbf{Eqn. 6}$$

Q_t, the quantity of solute adsorbed by the material at time t in mg.g^{-1} ; K_2, the apparent rate constant of the pseudo-second order in g.mg^{-1}.min^{-1}; Q_e, the adsorption capacity at equilibrium in mg.g^{-1}.

The plot of $\frac{t}{Q_t}$ as a function of time t gives a straight line with a slope equal to $\frac{1}{Q_e}$ and an intercept equal to $\frac{1}{K_2 Q_e 2}$.

2.4.3.3. Intra-particle diffusion model : Webber and Morris model (Omokpariola, 2021)

$$Q_t = K_{in} t^{1/2} + \mathrm{C} \qquad \textbf{Eqn. 7}$$

Q_t, the adsorption capacity at time t in mg.g^{-1}; K_{int}, the rate constant of intra-particle diffusion in mg.g^{-1}.min^{-1}; C, the constant related to the thickness of the boundary layer in mg.g^{-1}.

The plot of Q_t versus $t^{1/2}$ gives a straight line with a slope equal to K_{int} and an intercept equal to C.

2.4.3.4. Elovich model: Chien et al., 1980 (Omokpariola, 2021)

$$Q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} lnt \qquad \textbf{Eqn. 8}$$

Q_t, the adsorption capacity at time t in g.mg^{-1}; α, the initial adsorption rate in mg.g^{-1}.min^{-1}; β, the desorption constant in g.mg^{-1}.

The plot of Q_t as a function of lnt gives a slope of $\frac{1}{\beta}$ and an intercept equal to $\frac{1}{\beta} ln(\alpha\beta)$.

2.4.4. Modelling of adsorption isotherms

The following models, in their linear form, were used to describe the adsorption isotherms of BM on activated carbon.

2.4.4.1. Langmuir model

$$\frac{C_e}{Q_e} = \frac{1}{\mathrm{b}Q_{max}} + \frac{1}{Q_{max}} C_e \qquad \textbf{Eqn. 9}$$

Where Q_e is the amount of BM adsorbed at equilibrium in mg.g^{-1}, Q_{max} is the maximum amount adsorbed at monolayer saturation or maximum adsorption capacity in mg.g^{-1}, Ce is the weight concentration at equilibrium in mg.L^{-1}, and b is the Langmuir constant.

2.4.4.2. Freundlich model

$$lnQ_e = lnK_F + \frac{1}{n} lnC_e \qquad \textbf{Eqn. 10}$$

Q_e being the equilibrium adsorption capacity in mg.g^{-1}, C_e the equilibrium solute concentration in mg.L^{-1}, K_F and n: empirical constants (dimensionless) to be determined.

2.4.5. Thermodynamic parameters related to the adsorption process.

Knowledge of the amount of energy involved in the adsorption process is necessary for a complete characterization of the adsorbent. The amount of energy allows thermodynamic parameters such as entropy (ΔS°), standard enthalpy (ΔH°) and free enthalpy (ΔG°), which provide information on the degree of disorder at the adsorbate-adsorbent interface, the exothermicity or endothermicity of the adsorption process, and the spontaneity of the adsorption reaction, respectively. These parameters are determined using the following equations Eqn. 11, Eqn. 12, (13) and (14):

$$K_d = \frac{Q_e}{C_e} \quad \textbf{Eqn. 11}$$

Where K_d is the distribution coefficient in $L.g^{-1}$, Q_e is the amount of solute adsorbed per gram of adsorbent in $mg.g^{-1}$, C_e is the amount of solute in solution per litre of solution in $mg.L^{-1}$;
The change in free enthalpy is a function of the distribution coefficient and is obtained from the following formula (24):

$$\Delta G^{\circ} = -RTLnK_d \quad \textbf{Eqn. 12}$$

$\Delta G°$ being the change in free energy in $kJ.mol^{-1}$, R the ideal gas constant ($R = 8.314\ J.mol^{-1}.K^{-1}$), Kd the absolute temperature in K.
Free enthalpy is related to standard enthalpy and entropy by the following formula (25):

$$\Delta G° = \Delta H° - T\Delta S° \quad \textbf{Eqn. 13}$$

Which leads to:

$$LnK_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad \textbf{Eqn. 14}$$

$\Delta H°$ being the change in free enthalpy in $kJ.mol^{-1}$, $\Delta S°$ the change in free entropy in $kJ.mol^{-1}$.
The LnK_d curve as a function of $\frac{1}{T}$ is the straight line used to determine the value of standard entropy and enthalpy.

3. Results and Discussion

3.1. Pyrolysis yield

To determine the effect of impregnation on coal yield, the pyrolysis yields of raw shells and impregnated shells were compared. The results (**Figure 2**) show that impregnation increases the thermal resistance of the precursor material with a higher yield. This can be explained by the fact that phosphoric acid is a dehydrating agent that can delay thermal decomposition and thus limit mass losses. The value obtained (64.04%) is comparable to those reported in the literature and confirms the interest of using shells as a precursor material for the industrial production of activated carbons.

3.2. Physicochemical parameters of raw shells and activated carbon

To determine the properties of activated carbon, its physicochemical characterization was carried out in **Table 1**. Thus, to assess the influence of the process on the properties of the carbon, the latters were compared to those of the raw shells. The activated carbon has low water (6.66%) and ash (3.30%) contents, compared to 7.40% and 2.9% for the raw shells. These values are below the tolerable limits for activated carbon, which is 10% (Ouedrhiri *et al.,* 2018). This low ash content shows that it could be an excellent adsorbent, as ash is an inactive filler that reduces the performance of an adsorbent by clogging the pores and cluttering the adsorption surface. The methylene blue index (600.18 $mg.g^{-1}$) of the charcoal is much higher than that of the raw shells, which is 400.14 $mg.g^{-1}$. This difference shows the effectiveness of the activated charcoal production process in increasing the porosity of the shells. The high methylene blue indices (600.18 $mg.g^{-1}$) and iodine (793.75 $mg.g^{-1}$) indices of the activated carbon indicate a heterogeneous distribution of pores, highlighting the carbon's strong affinity for large and medium-sized molecules such as organic matter and dyes, and small molecules such as heavy metals.

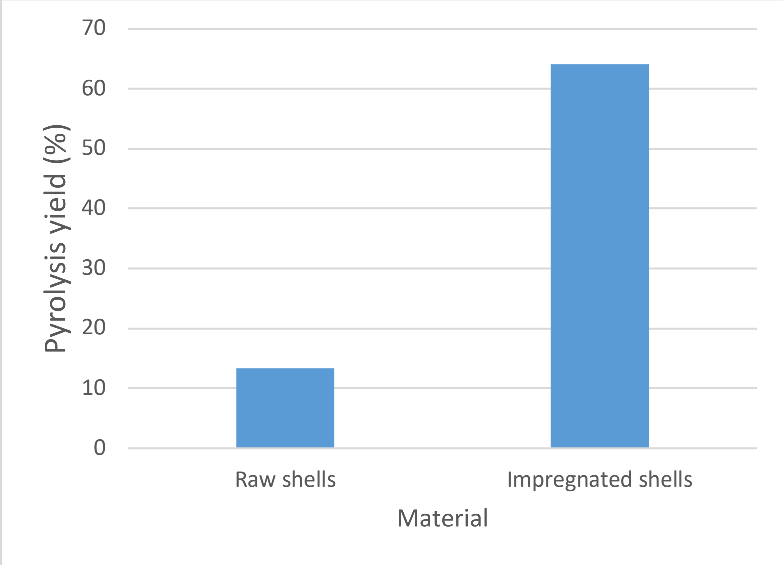

Figure 2. Pyrolysis yield of raw shells and impregnated shells

Table 1. Physicochemical parameters of the shells and activated carbon of *Balanites aegyptiaca*

Parameters	Units	Shells	Activated carbon
Yield	(%)	13.32	64.04
Moisture content	(%)	7.40	6.66
Methylene blue index	($mg.g^{-1}$)	400.14	600.18
Iodine index	($mg.g^{-1}$)	-	793.75

3.3. Optimisation of BM adsorption on activated carbon

3.3.1. Influence of contact time on BM adsorption

In order to determine the equilibrium time for BM adsorption on activated carbon, the change in the amount of BM adsorbed over time was monitored. The results (**Figure 3**) show that the curve can be broken down into two phases. A first, rapid phase between 0 and 30 minutes, during which the adsorption capacity of BM adsorbed increases significantly with contact time, rising rapidly from 0 to 47.92 $mg.g^{-1}$. The rapid adsorption during the first phase of the adsorption process can be explained by the availability of active sites on the surface of the adsorbent. A second, slower phase beyond 30 minutes, marked by a slight variation in the amount of methylene blue adsorbed until equilibrium is reached (45 min). On the other hand, the slight variation in adsorption capacity over time during the last phase of the adsorption process could be due to the gradual saturation of the adsorption sites.

.3.2. Influence of adsorbent weight on BM adsorption

To determine the influence of activated carbon mass on BM adsorption, changes in adsorption capacity were studied (**Figure 4**). It decreased from 18.47 to 6.54 $mg.g^{-1}$ for an increase in mass from 0.1 to 0.5 g. Above 0.5 g, the adsorption capacity of the carbon decreased slightly with mass. The value of 0.5 g was considered to be the optimal mass for the rest of the study.

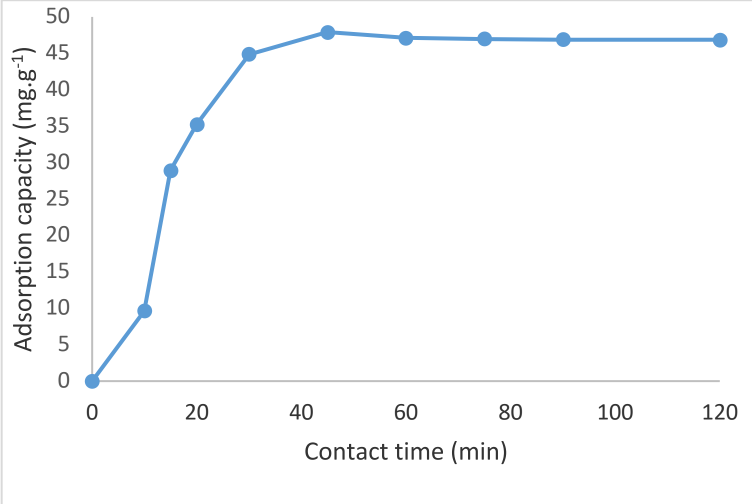

Figure 3. Change in methylene blue adsorption capacity over time
(V = 100 mL; CBM = 50 mg.L^{-1}; pH = 6.21; t = 120 min; T = 25 °C)

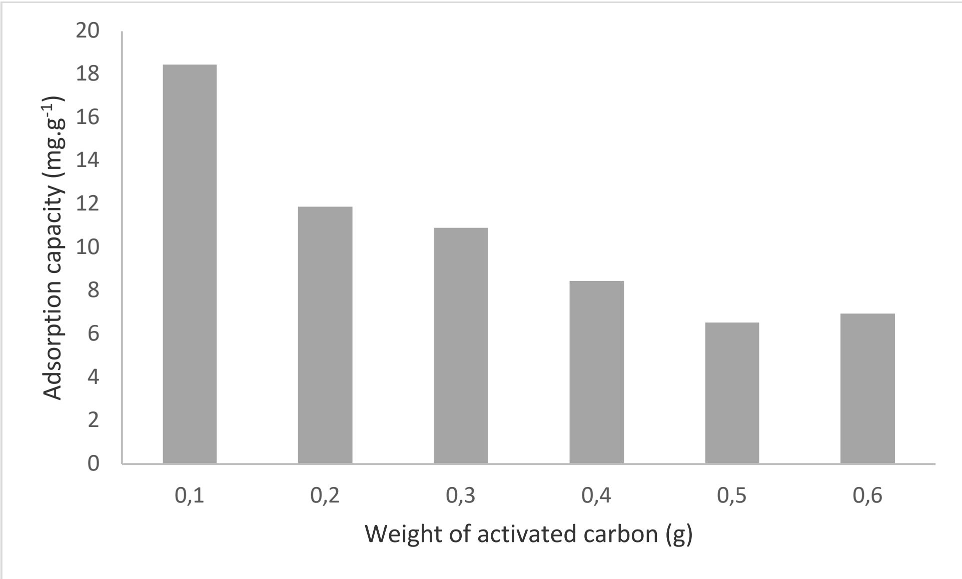

Figure 4. Influence of weight of activated carbon on BM adsorption capacity
(V = 100 mL; C= 50 mg.L^{-1}; pH=6.21; t= 120 min; T=25 °C)

3.3.3. Influence of initial BM concentration on BM adsorption

The initial concentration of the solution is also a parameter. Its impact on adsorption capacity was therefore studied (**Figure 5**). The results show that adsorption capacity increases slightly with the initial BM concentration.

3.4. Modelling of adsorption kinetics

To determine the kinetic model that best describes the adsorption of methylene blue on activated carbon, the three most widely studied kinetic models were applied, namely the pseudo-first-order model, the pseudo-second-order model and the intra-particle diffusion model (**Figures 6** and **7**). The kinetic parameters are calculated and summarised in **Table 2**. Both the pseudo-first order (R^2 = 0.9913) and pseudo-second order (R^2 = 0.9967) models can describe the adsorption of methylene blue on the surface of activated carbon. This highlights the simultaneous existence of physisorption and chemisorption. Nevertheless, the pseudo-second-order model is the model that best describes the adsorption of MB on the surface of activated carbon. This model is also generally the most widely used model to describe chemisorption phenomena. This is consistent with the literature, which reports that the kinetics of dye adsorption on adsorbents are consistent with the assumptions of the pseudo-second-order model, following the type of molecules that interact with the different functional groups on the surface of these adsorbents (Gueye, 2015; Kalidou & El Hadji Moussa, 2022). The high correlation coefficient associated with the intra-particle diffusion model (R2 = 0.9825) also indicates the existence of intra-particle diffusion phenomena that occur during the adsorption process.

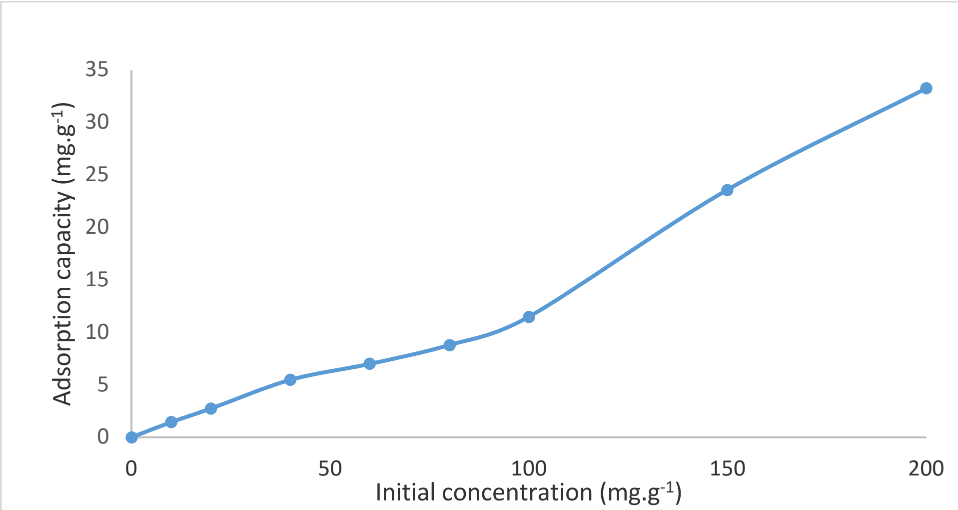

Figure 5. BM adsorption isotherm on activated carbon
(V = 100 mL; m= 0.5g; pH=6.21; t= 120 min; T=25 °C)

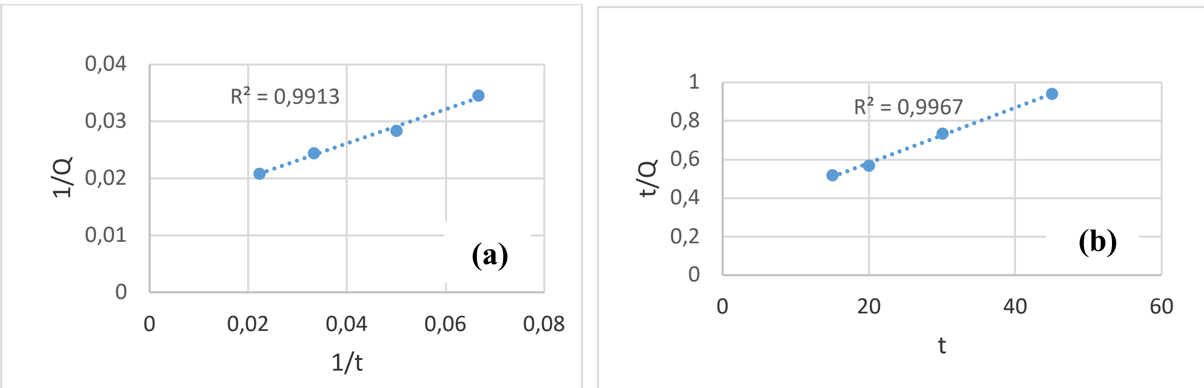

Figure 6. Pseudo-first-order (a) and pseudo-second-order (b) kinetic curves on activated carbon

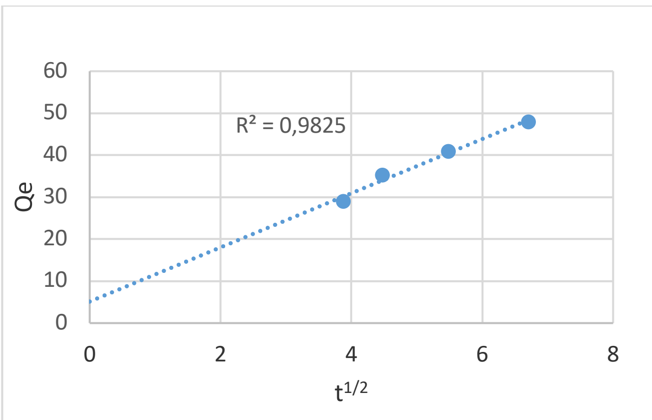

Figure 7. Intra-particle diffusion curve

Table 2. Kinetic parameters of the models studied

Parameters	Values
Pseudo premier ordre	
Q_e (mg.g^{-1})	70.92
K_1 (min^{-1})	21.27
R^2	0.9913
Pseudo second ordre	
Q^2	11.50
K_2 (g.mg^{-1}.min^{-1})	0.0042
R^2	0.9967
Diffusion intraparticulaire	
K_p (mg.g^{-1}.min^{-1})	33.10
C	0.19
R^2	0.9825

3.5. Modelling of MB adsorption isotherms on charcoal

To determine the isotherm model that best describes the binding of MB to activated carbon, the Freundlich and Langmuir models were applied (**Figure 8**).

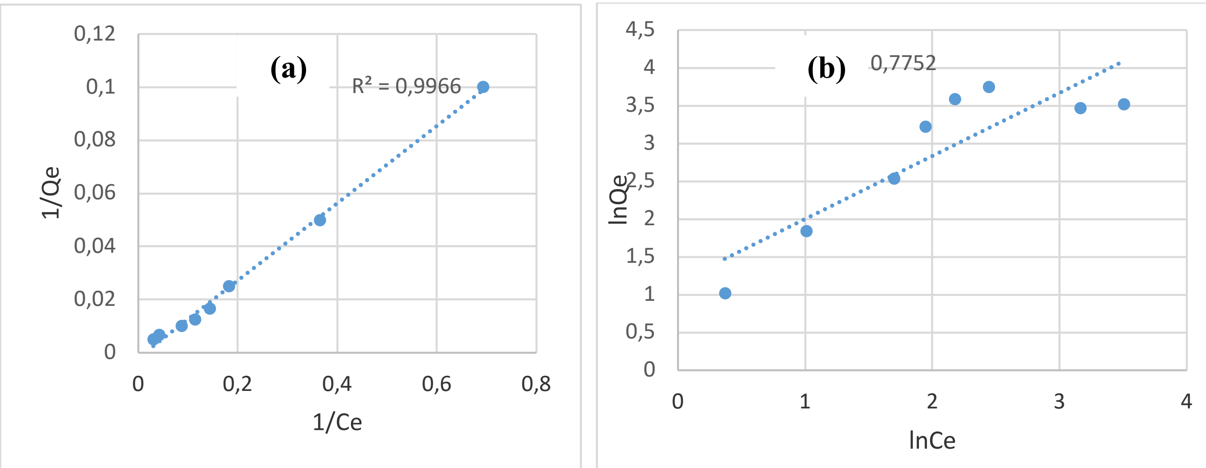

Figure 8. Langmuir (a) and Freundlich (b) models

The parameters of the isotherms studied are calculated and summarised in **Table 3**. The results obtained show that the Langmuir model is the model that best describes the adsorption of MB on activated carbon. This shows that the binding of MB to the adsorption sites is of the chemisorption type and occurs through the formation of a monolayer. Similar results have been reported by several authors (Ahsaine *et al.*, 2018; Gueye, 2015). The maximum adsorption capacity calculated from the Langmuir model is 9.42 mg.g^{-1}, showing good affinity with MB. The specific surface area calculated from the Langmuir model is 357.15 m².g^{-1}. The Freundlich constant K_f 0.8572 mg.g^{-1} shows a moderate affinity of the carbon for MB. The Freundlich isotherm constant n (2.0593) between 1 and 10 shows that the binding of MB to activated carbon is favorable. The heterogeneity factor 1/n (0.4856) less than 1 shows that the interface between activated carbon and methylene blue is favorable for adsorption (Akartasse *et al.*, 2022; Ouzani *et al.*, 2025)

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Table 3. Parameters of the isotherms studied

Parameters	**Units**	**Values**
	Freundlich isotherm	
K_F	$mg.g^{-1}$	0.8572
1/n	-	0.4856
N	-	2.0593
R^2	-	0.7752
	Langmuir isotherm	
Q_{max}	$mg.g^{-1}$	9.4243
B	$L.mg^{-1}$	0.4743
R_L	-	0.0516
R^2	-	0.9966
S	$m^2.g^{-1}$	357.15

3.6. Thermodynamic study of BM adsorption on activated carbon

To determine the nature of adsorption, thermodynamic parameters such as free enthalpy (ΔG°), standard enthalpy (ΔH°) and entropy (ΔS°) were identified (**Table 4**). The free enthalpy, ΔG°, is negative at all temperatures, showing that the adsorption of methylene blue onto activated carbon is a spontaneous process. The decrease in ΔG° with temperature proves that adsorption is more favorable at low temperatures. However, the negative value of enthalpy, ΔH°, shows that the process is exothermic. The negative value of entropy, ΔS°, indicates a decrease in disorder at the solid-liquid interface during the adsorption process.

Table 4. Thermodynamic parameters of BM adsorption on activated carbon based on *Balanites aegyptiaca*

Parameters	**Units**	**Temperatures (°C)**			
		30	60	80	100
ΔG°	$kJ.mol^{-1}$	- 4.30	-4.82	-6.59	-8.83
ΔH°	$kJ.mol^{-1}.K^{-1}$	-9.34			
ΔS°	$kJ.mol^{-1}$	0.34			

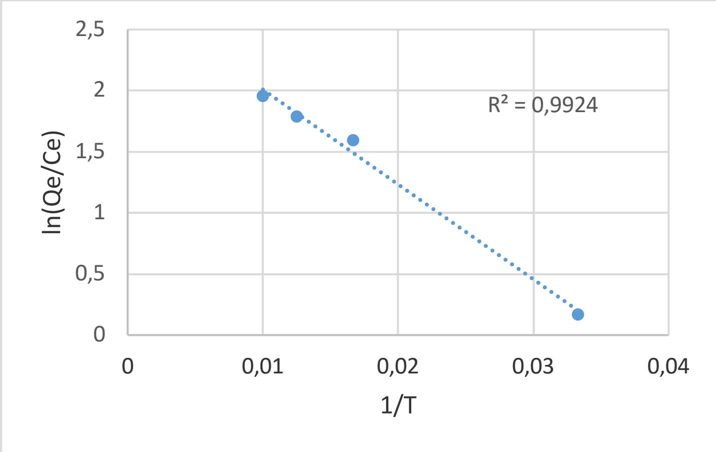

Figure 9. Van't Hoff model

Conclusion

The goal of this study was to recycle *Balanites aegyptiaca* shells by producing activated carbon, which is effective for treating wastewater containing dyes such as Methylene Blue (MB).

The results obtained showed that the activated carbon produced is characterized by highly developed porosity, as showed by high methylene blue (600.18 $mg.g^{-1}$) and iodine (793.75 $mg.g^{-1}$) indices.

The effectiveness of activated carbon in removing methylene blue from aqueous solutions was studied. The influences of parameters such as the mass of the adsorbent, the initial concentration of methylene blue in the solution, the temperature and the contact time were investigated. The results have showed that the optimal conditions for the adsorption of methylene blue onto activated carbon correspond to a carbon mass of 0.5 g, an initial concentration of 100 $mg.L^{-1}$, a contact time of 60 min and a temperature of 30°C. The kinetic study showed that the adsorption of methylene blue (MB) onto the surface of activated carbon is best described by the pseudo-second-order model. The study of adsorption isotherms has showed that the adsorption of MB on activated carbon is best described by the Langmuir model. The maximum adsorption capacity of activated carbon calculated using the Langmuir model is 9.42 $mg.g^{-1}$. The calculated thermodynamic parameters have showed that the adsorption of methylene blue on activated carbon is a spontaneous and exothermic process.

Overall, this study has showed that *Balanites aegyptiaca* shells, considered waste during the fractionation of seeds for vegetable oil production, are an excellent precursor to produce activated carbon that can be used to treat industrial effluents containing dyes. Nevertheless, it would also be interesting to evaluate the performance of activated carbon for the removal of heavy metals, pesticides, wastewater having several types of pollutants, industrial wastewater, etc.

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