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Effect of the nature of the activating agent on the performance of activated carbons prepared from neem seed hulls (*Azadirachta indica* A. Juss): application to the elimination of methylene blue in aqueous solution

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Abstract
The treatment of industrial effluents is essential to combat environmental pollution. Activated carbon adsorption is one of the most widely used techniques for the treatment of dye-laden effluents. However, the efficiency of this process depends on the nature of the precursor material and the properties of the carbon used. The aim of this study is to determine the effect of the nature of the activating agent on the adsorbent properties of activated carbon based on neem shells. Three activated carbons (CA-H_3PO_4, CA-KOH and CA-$ZnCl_2$) were chemically prepared by using, respectively, H_3PO_4, KOH and $ZnCl_2$ as activating agents. The characterization of the active carbons produced included the determination of moisture and ash content, bulk density, surface functions and methylene blue and iodine indices. The CA-KOH gives the best adsorption capacity (35.23 $mg.g^{-1}$) of methylene blue while the CA-$ZnCl_2$ is more efficient for iodine adsorption (732.76 $mg.g^{-1}$). However, the CA-H_3PO_4 has a cumulative efficiency for both small and large molecules. The results also showed that the prepared carbons are effective for the removal of methylene blue in aqueous solution. The kinetic study showed that the fixation of methylene blue on the studied adsorbents is best described by the pseudo-second order model. Finally, this study showed that the properties of the activated carbon are strongly influenced by the nature of the activating agent and that chemical activation makes it possible to obtain excellent activated carbons based on neem seed hulls which can be used in the treatment of industrial influent

1. Introduction

The increasingly sustained demographic growth in certain African large cities in general, and in Dakar in particular, leads to the discharge of large quantities of effluents loaded with various types of pollutants. These pollutants can be organic matter [1, 2], dyes [3, 4], heavy metals [5, 6], pesticides [7, 8], pharmaceutical compounds [9-11], hydrocarbons [12, 13], etc. Wastewaters management has

therefore become a major concern for polluting communities and companies. Thus, water decontamination is necessary to protect the environment. Several techniques have been developed to eliminate recalcitrant molecules in water, such as coagulation-decantation [14, 15], filtration [16, 17], adsorption, electrocoagulation, ion exchange [18], reverse osmosis [19], biosorption, etc. Adsorption on activated carbon is the most widely used technique. This process efficiency depends on the performance of the adsorbent used. The adsorption properties of an activated carbon are strongly influenced by the nature of the precursor on the one hand, and by the operating parameters used during its preparation on the other hand. Among these parameters, the most influential are the nature, the concentration and the impregnation ratio of the activating agent [20, 21], the temperature and time of pyrolysis [22], etc. The nature of the activating agent is one of the most important parameters of the activation process [23-25]. Several activating agents are known to be effective for the activation of activated carbons. Among these chemical agents, we can mention potassium hydroxide [26, 27], zinc chloride [27], phosphoric acid [26, 27], potassium carbonate [28], calcium chloride [29] and sodium hydroxide [28], etc. This study has a double aim. First it will determine the adsorbent properties of different activated carbons prepared with various activating agents (H_3PO_4, KOH and $ZnCl_2$) and then, compare their performances to remove a dye (methylene blue) in aqueous solution.

2.1. Preparation of adsorbents

2.1.1. Preparation of the raw material

The raw material used in this study is neem seeds collected in Babol, Kaolack region, (Senegal). After collection, the seeds were dried. We proceeded by hand sorting to remove impurities and foreign particles. And then, we did manual hulling to separate the hull from the kernel. The resulting hulls were washed thoroughly with distilled water to remove dust and other water-soluble compounds and then oven dried at 105°C for 24 hours. The dried hulls were ground into fine particles using an electric knife mill (Saachi NB-0002) and sieved. Only particles with a diameter less than 800 µm are retained for the preparation of activated carbons.

2.1.2. Preparation of activated carbons

The different activated carbons have been prepared from neem hulls by chemical means using three activating agents, H_3PO_4 (85%), $ZnCl_2$ (20%) and KOH (20%) and named CA- H_3PO_4, CA- $ZnCl_2$ and CA-KOH, respectively. The preparation process is the same for all activated carbons and is inspired by the work of TCHAKALA et al [30]. Neem seed hull powders are mixed with the activating agent at an impregnation ratio (precursor weight/activating agent weight) equal to 1/2 [24, 31]. The mixture is stirred for a sufficient time at room temperature (about 25°C) to ensure a good diffusion of the activating agent within the material matrix. The mixture is then placed in an oven at a temperature of 120°C for 6 hours. The impregnated particles are then carbonized in an oven at a temperature of 450°C for 2 h. The activated carbons thus obtained are washed with distilled water to eliminate the residues of the activating agent and other impurities until a washing water of neutral pH is obtained. Finally, the carbons are dried in an oven at 105°C for 24 hours and then stored in plastic jars.

2.2. Preparation of the adsorbate

In this study, Methylene Blue (MB), a methylthioninium chloride showed in **Figure 1**, has been used to prepare the wastewaters to be treated. The dye stock solution has been prepared by dissolving 1 g of dye in 1 L of distilled water and solutions of desired dye concentrations were obtained by diluting the stock solution.

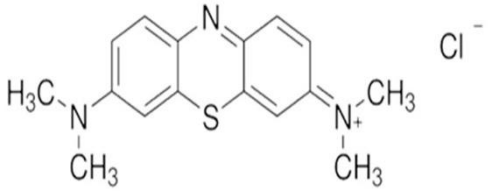

Figure 1. Methylene blue structure

2.3. Determination of the pyrolysis yield

The pyrolysis yield reflects the weight loss of the biomass during pyrolysis. It is calculated using the following relationship (1):

$$R = \frac{Mf}{Mi} * 100 \qquad \textbf{(Eqn. 1)}$$

R represents pyrolysis yield in %; M_f, the final weight of coal in g; M_i, the initial weight of precursor material (g).

2.4. Determination of the physico-chemical parameters of the different activated carbons

2.4.1. Determination of the pH

The pH is determined according to the ASTM 3838-80 method. A mass of approximately 1 g of carbon is introduced into 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).

2.4.2. Determination of humidity

The moisture content is determined according to the standard (NF V 03- 603) by the loss in weight of a sample of approximately 1 g that has been oven-dried at 105°C until a constant mass is obtained.

2.4.3. Determination of mineral content

The Mineral Matter (MM) content, or ash, is determined by weight loss from the dry matter by incinerating it in an electrically heated muffle furnace at approximately 550°C for three hours (NF V 03-922). The sample is then cooled in a desiccator and weighed as soon as the laboratory temperature is reached.

2.4.4. 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 weight of the sample and the bulk volume of the sample.

2.4.5. Determination of the iodine value

The iodine molecule has been chosen as a reference molecule to evaluate the adsorption capacity of solutes of small molecular size <10 Å [32]. The iodine value is defined as the amount, in milligrams of iodine, adsorbed by 1 g of adsorbent. The iodine value is determined according to the AWWA B 600-78 method [26]. A known weight of activated 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 min before being filtered. The filtrate is assayed with a sodium thiosulphate solution using starch as a colour indicator.

2.4.5. Determination of the methylene blue value

We have taken methylene blue as a reference molecule to evaluate the adsorption capacity of solutes of size >15 Å [32]. In other words, the methylene blue index is considered as a basis for measuring 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 for its determination is inspired by the work of DAS [33]. A weight of approximately 1 g of previously dried charcoal is brought into contact with 50 mL of a methylene blue solution of concentration 200 mg. L^{-1} for 30 min under continuous stirring. After adsorption, the residual methylene blue concentration is measured using a UV spectrophotometer (Agilent Technologies Cary 60 UV-Vis) at a wavelength (λ= 654 nm). The methylene blue index is calculated using the following formula (2):

$$I_{BM} = \frac{(C_i - C_f)V}{m_{CA}} * 100 \quad (\mathbf{Eqn.2})$$

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

2.4.6. Estimation of surface functions

The determination of the surface functions was carried out according to the BOEHM method which corresponds to an acid-base titration. The basic groups on the surface of the activated carbons are globally determined, while the acid groups are determined separately. Weight of approximately 0.1 g of shell are brought into contact with 50 mL of each of the aqueous solutions of NaOH and HCl of molar concentration 0.01 M. Each mixture is stirred for 24 hours in order to ensure that the maximum number of surface groups has reacted. The suspensions are then filtered and 10 mL of the filtrate from each solution is assayed. The basic solution was determined with 0.01 N hydrochloric acid and the acidic solution with 0.01 N sodium hydroxide. The surface functions sought are expressed in milliequivalents per gram of adsorbent ($m\text{-}eq.g^{-1}$).

2.5. Adsorption of methylene blue on neem hulls

The adsorption tests have been carried out in a stirred batch reactor, in 250 mL Erlenmeyer flasks, by bringing a known weight of activated carbon into contact with a solution with a well-defined methylene blue concentration. The assembly was kept under continuous stirring at a speed of 400 rpm for a defined time at room temperature (about 25°C). After each adsorption test, the solution is filtered on filter paper and the filtrate is analysed to determine the residual methylene blue concentration using a spectrophotometer (UV-Vis 60 Cary 60 Agilent Technologies). The adsorption capacity and the removal rate are calculated respectively, according to the following equations (3) and (4):

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

$$T = \frac{(C_i - C_f)}{C_i} * 100 \quad (\mathbf{Eqn.4})$$

Q_e represents the adsorption capacity in $mg.g^{-1}$; C_i, the initial concentration of MB in $mg.L^{-1}$; C_f, the concentration of the solution after adsorption in $mg.L^{-1}$; V, the volume of the solution in L; T, the rate of elimination of MB in %.

2.5.1. Effect of the nature of the activating agent on the elimination kinetics of methylene blue

To study the effect of the nature of the activating agent on the adsorption kinetics and thus determine the equilibrium adsorption capacity for each adsorbent, we followed the evolution of the quantity of methylene blue adsorbed as a function of time (0 to 180 min). The effect of the nature of the activating

agent on the kinetics was carried out under the following conditions: the initial concentration of MB in the solution was fixed at 50 mg.L^{-1}, the volume of the solution at 100 mL, the mass of adsorbent at 0.1 g, the temperature at 25°C and without adjustment of the pH of the initial MB solution prepared.

2.5.2. Modelling the adsorption kinetics of methylene blue

To determine the equilibrium adsorption capacity as well as the adsorption mechanism, the following four models were tested: the pseudo-first order model, the pseudo-second order model, the intra-particle diffusion model and the Elovich model.

2.5.2.1. Pseudo-first order model : Lagergren model [26]

$$\frac{1}{Q_t} = \frac{1}{Q_e} + \frac{K_1}{Q_e}\frac{1}{\mathrm{t}} \qquad (\mathbf{Eqn.\,5})$$

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

The plot of $\frac{1}{Q_t}$ as a function of $\frac{1}{\mathrm{t}}$ gives a straight line with a slope equal to $\frac{K_1}{Q_e}$ and an intercept equal to $\frac{1}{Q_e}$.

2.5.2.2. Pseudo-second order model : HO and Mckay model [34]

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e 2} + \frac{1}{Q_e}t \qquad (\mathbf{Eqn.\,6})$$

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 $\frac{1}{K_2 Q_e 2}$.

2.5.2.3. Intra-particle diffusion model : Webber and Morris model [34]

$$Q_t = k_{int}t^{1/2} + C \qquad (\mathbf{Eqn.\,7})$$

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.

2.5.2.3. Elovich model : Chien et al. [35]

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

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 $\frac{1}{\beta} ln(\alpha\beta)$.

3. Results and discussion

3.1 Pyrolysis yield of the activated carbons produced

The yield provides information on the mass losses in relation to the initial mass of the precursor during pyrolysis. The results obtained **(Figure 2)** show that the impregnation of the precursor material by the

activation agents used makes it possible to increase the pyrolysis yield compared to the unimpregnated precursor (CA-NI). In other words, the impregnation increases the thermal resistance of the precursor material. This can be explained by the fact that the activating agents used are dehydrating agents that can delay thermal decomposition and limit the loss of carbon atoms in the form of volatile matter (CO, CO_2, CH_4, etc.) and tars. The results obtained also indicate that the pyrolysis yield depends on the nature of the activating agent used. Phosphoric acid gives the best pyrolysis yield, followed by potassium hydroxide and zinc chloride. This result complies with the literature [26, 36, 37].

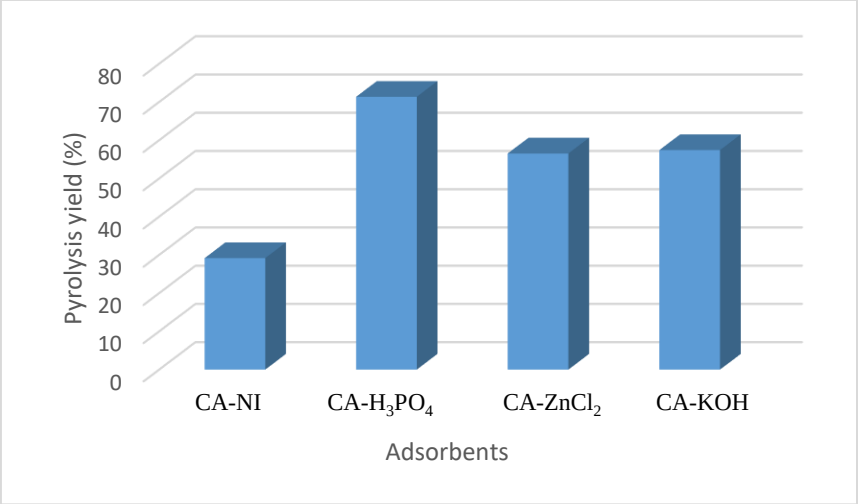

Figure 2. Pyrolysis efficiency of different adsorbents

3.2. Determination of the physico-chemical parameters of the different adsorbents

3.2.1. Determination of the surface functions of the adsorbents

To determine the nature of the functional groups on the surface of the adsorbents, we determined the surface functions of the adsorbents. The obtained results showed in **Table 1** reveal that CA-H_3PO_4 contains more acidic functions than the other adsorbents, while the surface of CA-KOH is naturally more basic than that of the other adsorbents. These results confirm that the surface of the carbon is very influenced by the nature of the activating agent.

Table 1. Surface functions of the studied adsorbents (m-eq.g^{-1})

Activated carbon	Basic fonctions	Acid fonctions
CA-H_3PO_4	0.65	4.70
CA-$ZnCl_2$	1.10	4.30
CA-KOH	2.40	2.35

3.2.2. Determination of the physico-chemical parameters of activated carbons

To determine the adsorbing properties of the different carbons, their physico-chemical parameters were first determined. The obtained results **(Table 2)** show that the activated carbons have low ash and humidity levels. A high ash content has the effect of reducing the adsorption capacity of the activated carbon because the ash constitutes an inert mass that can obstruct the pores, thus leading to a reduction in adsorption capacity [26]. CA-$ZnCl_2$ has the highest ash content followed by CA-H_3PO_4. The low ash content (1.58%) of CA-KOH is explained by the fact that KOH reacts with the ash to give a soluble form that **may** be removed during washing [38]. The results also show that the bulk densities of the different adsorbents are higher than the limiting bulk density (0.25 g.cm^{-3}) defined by the American Water Works Association (AWWA) [38]. The results shown also that $ZnCl_2$ gives the higher bulk density, while H_3PO_4 is the least dense activated carbon. The outcomes also show that CA-KOH has

the best methylene blue value and the lowest iodine value while the opposite is observed for CA-$ZnCl_2$. However, CA- H_3PO_4 displays both high methylene blue and iodine values due to the fact that activation with H_3PO_4 favours a heterogeneous pore size distribution. The results show that chemical activation develops porosity and makes the material surface more reactive. This leads to an improvement in the adsorbent properties of activated carbons. The results confirm that the performance of the carbon depends on the nature of the activation agent used, particularly due to the difference in reactivity of the activation agents used.

Table 2. Physico-chemical parameters of the different adsorbents studied

Parameters	Units	CA-H_3PO_4	CA-KOH	CA- $ZnCl_2$
pH	-	2.68	6.98	7.14
Humidity	%	2.80	3.64	0.86
Ash content	%	2.29	1.58	3.19
I_{I2}	$mg.g^{-1}$	730.45	617.00	732.76
I_{BM}	$mg.g^{-1}$	17.26	17.68	9.67
Bulk density	$g.cm^{-3}$	395.76	438.40	464.86

3.3. Adsorption of methylene blue on activated carbon

3.3.1. Adsorption kinetics of methylene blue on activated carbon

To determine the effect of the nature of the activating agent on the performance of the activated carbon, we have studied the kinetics of the adsorption of BM. The results **(Figure 3)** showed that the amount of MB adsorbed increases as expected with time for all adsorbents. The evolution of the quantity of MB adsorbed follows the same pattern and comprises two phases for all the carbons studied.

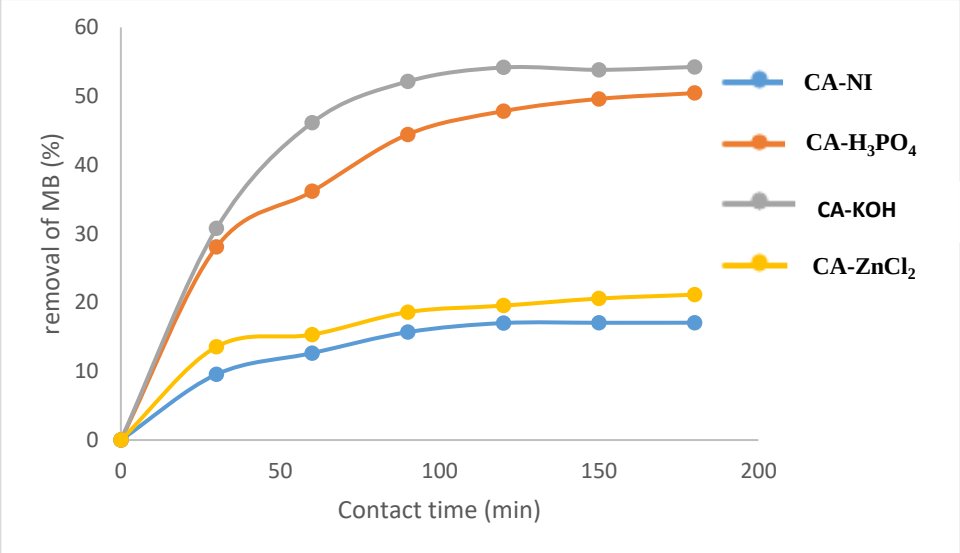

Figure 3. Effect of the nature of the activating agent on the capacity of BM as a function of contact time (C_{BM}= 50 $mg.L^{-1}$; pH=6,21; T=24 °C; m=0,1 g)

There is a first rapid phase where the quantity of MB increases rapidly and significantly, and then a second one, less rapid, marked by a slight variation in the quantity of methylene blue adsorbed until equilibrium is reached. This pattern can be explained by the fact that the number of active sites on the surface of the carbon is higher at the beginning of the adsorption process and decreases with contact

time and with the number of occupied sites. The results also show that the equilibrium time depends on the nature of the activation agent used. The equilibrium time is shorter for CA-KOH (120 min) than for CA-H_3PO_4 and CA-$ZnCl_2$ for which it reaches 150 min. This difference in equilibrium time may be due to the difference in structure of the adsorbents [39]. The adsorption capacities obtained show that CA-KOH has the best adsorption capacity (54.17 $mg.g^{-1}$) followed by CA- H_3PO_4 (49.6 $mg.g^{-1}$). In sum, the results show that activated carbons are more effective than the carbon obtained without impregnation and its effectiveness depends on the nature of the activating agent.

3.3.1.2. Modelling of adsorption kinetics

In order to determine the best kinetic model of MB adsorption and to know the mechanism of methylene blue fixation on the adsorbents, we applied the following kinetic models such as: the pseudo first-order model, the pseudo-second order model, the intra-particle diffusion model and the Elovich model. The obtained kinetic models are shown in **Figures 4** and **5** and the calculated kinetic parameters are shown in **Table 3. Figures 4** and **5** show that the pseudo-second order model is the most suitable model to describe the adsorption of MB on all studied carbons. We can therefore conclude that the fixation of methylene blue to these adsorbents is of the chemisorption type.

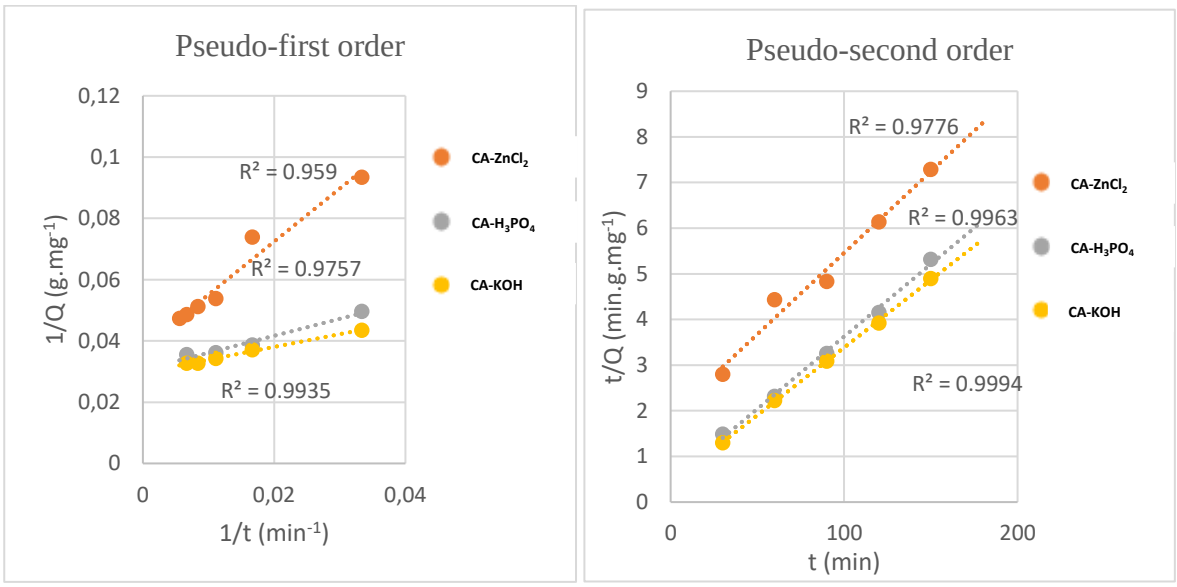

Figure 4. Kinetic models of the pseudo-first and pseudo-second order of MB adsorption on the studied adsorbents

The affinity of MB adsorption to the pseudo-second order model is consistent with the results of GUEYE et al. 2015, who worked on BM adsorption on a peanut shell-based activated carbon [26], with those of BHATTACHARYA et al. 2006, who worked on zinc adsorption on different adsorbents [40]. The low values of the correlation coefficients of the intra-particle diffusion and Elovich models of CA-H_3PO_4 and CA-$ZnCl_2$ show that the adsorption process of MB on these supports is not well described by these models. For CA-KOH, the high correlation coefficients of the models studied show that these models describe well the fixation of MB on this carbon. The results also show that the adsorption mechanism depends on the nature of the activating agent. The fixation rates 0.0022 $g.mg^{-1}.min^{-1}$ and 0.0020 $g.mg^{-1}.min^{-1}$ of MB respectively, for CA-KOH and CA- H_3PO_4 are very close and higher than that of CA-$ZnCl_2$ (0.0006 $g.mg^{-1}.min^{-1}$). This result can be explained by the difference in porosity highlighted by the methylene blue and iodine indices.

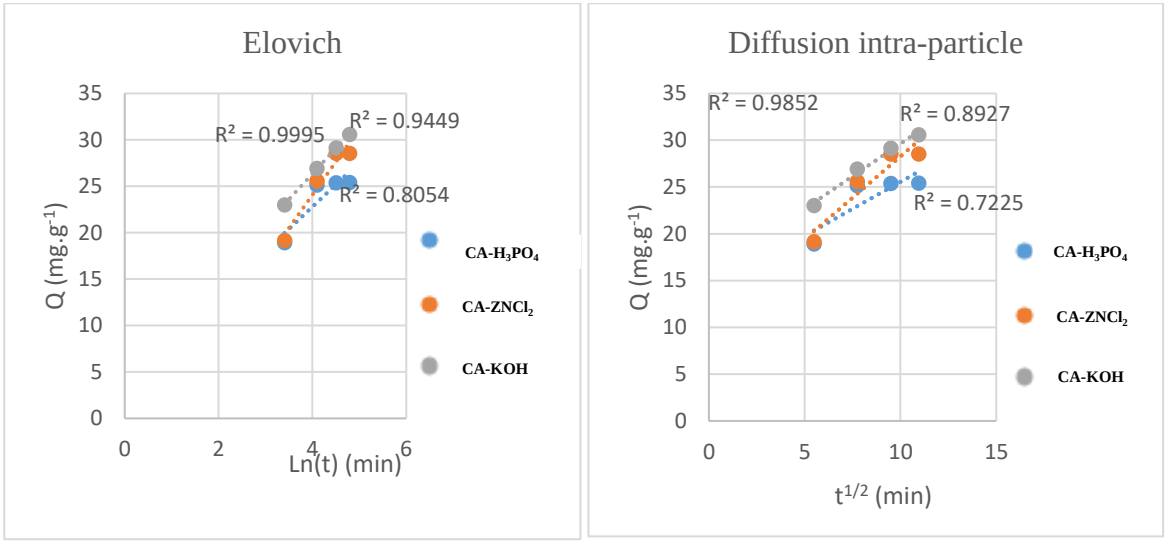

Figure 5. Kinetic models of intra-particle diffusion and Elovich adsorption of MB on the studied adsorbents

Table 3. Kinetic parameters of MB adsorption on the studied adsorbents

Parameters		**CA-H_3PO_4**	**CA-$ZnCl_2$**	**CA-KOH**
		Pseudo-first order		
Q_e	$mg.g^{-1}$	32.68	26.46	33.67
K_1	min^{-1}	18.12	45.78	17.39
R^2	-	0.973	0.959	0.9935
		Pseudo-second order		
Qe	$mg.g^{-1}$	31.54	28.09	33.78
K_2	$g.mg^{-1}.min^{-1}$	0.0022	0.0006	0.0020
R^2	-	0.9963	0.9776	0.9994
		Intra-particle diffusion		
K_{int}	$mg.g^{-1}.min^{-1}$	1.15	1.77	1.39
C	-	14.01	10.57	15.73
R^2	-	0.7225	0.8927	0.9852
		Elovich		
α	$mg.g^{-1}.min^{-1}$	5.89	8.21	6.58
β	$g.mg^{-1}$	0.21	0.14	0.18
R^2	-	0.8054	0.9449	0.9995

Conclusion

Neem seed hulls, once considered as a waste product, can be valued through the production of activated carbons, which can be used to remove of recalcitrant molecules in the case of wastewaters treatment. The aim of this study is first to prepare activated carbons by chemical means using various activating agents such as H_3PO_4, KOH and $ZnCl_2$ and then to study the effects of the activating agent on the pyrolysis yield and on the adsorbent properties of the produced activated carbon. The results of the characterization showed that the properties of the activated carbon are strongly influenced by the nature of the activating agent. Indeed, CA-KOH presents the best adsorption capacity for methylene blue (17.68 $mg.g^{-1}$) while ZnCl2 is more efficient for the adsorption of iodine (732.76 $mg.g^{-1}$). The kinetic study showed that the fixation of methylene blue on the adsorbents is perfectly described by the pseudo-second-order model, thus showing that the adsorption is of chemisorption type. Finally, this study has shown that neem seed hulls, a lignocellulosic waste, available and at low cost, can constitute an

excellent precursor for the production of activated carbons, usable in wastewater treatment and that the choice of the activating agent constitutes a key factor in the efficiency of the adsorption process. The evaluation of the effects of other influential parameters such as impregnation ratio, time and temperature of pyrolysis on the adsorption properties of the carbon will help to improve its performances.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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