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EXPERIMENTAL STUDY OF THE ADSORPTION OF METHYL RED ON COAL FROM THE SHELL OF THE COCOA POD

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Abstract

The adsorption of pollutants by coal from agricultural waste is a promising way of depollution of the environment. This is due to the affordable production cost and efficiency of coal. This research work focuses on the adsorption of methyl red on coal from cocoa pod shell. In this work, the contact time, the effect of pH and the quantity of initial material on the adsorption kinetics of methyl red were analysed. The experimental results of the adsorption of methyl red on this coal have been applied to kinetic models and adsorption isotherms. The cocoa pod shells were ground using Retsch SK100 mills. Pyrolysis was carried out at 400°C in a muffle furnace of the Nabatherm 30-3000°C type. The maximum adsorption capacity (q_m) of the methyl red dye was 12.232 mg/g. And the equilibrium time was found at 40 minutes. This maximum adsorption capacity varies from 7.536 to 27.544 mg/g with a variation in the quantity of material from 0.002 to 0.018 moles. The same applies to the pH. From pH = 3.56 to pH = 10, the maximum adsorption capacity of methyl red varies from 6.39 to 13.88 mg/g. The results obtained show that basic pH allows for better removal efficiencies. With a correlation coefficient of 0.9986, the kinetic adsorption profile was well described by the pseudo-second order model. With a correlation coefficient of 0.9937, the adsorption equilibrium was well described by the Langmuir isotherm model.

Key words: adsorption, cocoa shell pod, coal, kinetic, methyl red

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1. Introduction

Environmental pollution such as water pollution by multiple chemical substances, the emission of certain gases into the atmosphere and the discharge of toxic effluents into natural environment remains a major concern for the ecosystem.

In Côte d'Ivoire, traces of pesticides, heavy metals and polychlorinated biphenyls (PCBs) have been found in fish of the Ebrié and Grand-Lahou lagoon (Adingra et al., 2011; Hampoh et al., 2014). In addition, there is a lack of a plan to protect natural waters against this pollution. This absence can contribute to the degradation of the quality of these waters and to the increase of certain undesirable mineral and organic micropollutants in water intended for consumption (Afoufou and Achour, 2002). Hence this situation provides the explanation for the presence of these substances in the human organism. Indeed, the work of Traoré et al. (2002) showed that the breast milk of women in the Buyo zone contains organochlorine pesticide residues. Moreover, 24% of current diseases in the world can be attributed to environmental pollution, according to Maamri (2017).

That is why appropriate solutions to remedy this state have been sought in recent years and remain imperative. Various treatment methods have been applied for the removal of dyes from contaminated wastewater including advanced oxidative process, photocatalysis, membrane filtration, adsorption and

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electrochemical degradation (Bouafia, 2010; Jawad and Abdulhameed, 2020a). Among these methods, adsorption is a promising approach due to its simple operation design, non-susceptibility to pollutants, reusability, high efficiency, low-cost, and lower waste production (Bhaumik and Mondal, 2013; Jawad and Abdulhameed, 2020a). Adsorption is a surface phenomenon by which molecules attach themselves to the surface of the adsorbent by weak bonds: van der Waals forces, electrostatic interactions, hydrogen bonds. These adsorbents include a variety of materials such as: activated coals (Bhaumik and Mondal, 2013; Jawad and Abdulhameed, 2020a; Kouadio et al., 2019), Chitosan/ activated coals (Jawad et al., 2020a) chitosan, zeolites (Jawad et al., 2020b; Mohammed et al., 2020), Acid-factionalized biomass material (Jawad et al., 2020c), Iraqi red kaolin (Jawad and Abdulhameed, 2020b), silica gels, activated clays (or bleaching earths), activated alumina (Adnanen and Bentayeb, 2015).

Currently, this method uses more and more materials from natural waste of agricultural origin, often little or poorly recovered but easily accessible for the elimination of pollutants, including dyes (Benaissa, 2012). This agricultural waste can be used raw, transformed into a functionalized material or into activated carbon. However, a previous study has shown that the shell of raw cocoa pods has high swelling values and water retention capacity. These values are 2.4 and 3.7 g.g-1 respectively. These high values indicate that this material retains a high amount of water. And this could be a limiting factor as to the adsorption capacity of the dyestuffs as it would cause clogging effects. In addition, this material has fewer porous structures with smaller diameters (Kokora et al., 2018). Furthermore, the favourable adsorption properties of a coal are generally related to its relatively large specific surface area, high adsorption capacity and high porosity, mechanical strength, thermal stability and abundance of functional groups. Concerning, coal from the shell of cocoa pods of the Forastero type, a study carried out by Kouadio et al. (2019) indicates a predominantly acidic surface, a specific surface between 475.76 and 588.25 m/g, a mesoporosity of 73.54 to 104.56 mg/g and a microporosity between 507 and 659 mg/g. With these relatively high values, this coal, produced at temperatures between 400 and 500°C without impregnation in a chemical substance, would be suitable for the removal various pollutants of the environment.bMoreover, the use of cocoa pod shells for coal production would be cheaper because they only undergo carbonization.

Moreover, they are sufficiently available and free of charge on the plantations. Cocoa pod shells represent 52-56% of the mass of a ripe pod. These cocoa residues are estimated at around 13 to 15 million tonnes. This material is therefore an asset for the elimination of pollutants, particularly methyl red.

Methyl red (2'-carboxy-4-N,N-dimethylamino-azobenzene) is an azo dye with structure similar to methyl yellow (dimethylamino-azo-benzene) that is a "potent liver carcinogen" (So et al., 1990). Methyl red is a dye mutagen; also, methyl red can be converted to the mutagenic metabolite N,N-dimethyl-p-phenylene diamine (So et al., 1990).

Thus, the general objective of this work is to study experimentally the removal of methyl red dye from water by adsorption on coal from cocoa pod shells. This was done according to the following specific objectives:

- study of some adsorption parameters
- application of kinetic models to the experimental results of the adsorption of methyl red by coal,
- application of adsorption isotherms to the mechanism of adsorption of methyl red by coal.

2. Material and methods

2.1. Material

The instruments used include laboratory glassware, chemicals and apparatus. The glassware is composed mainly of: beakers, Erlenmeyer flasks, graduated burette, graduated flask, wash-bottle, pipette, sieve, crucible, etc. The reagents used are: Methyl red ($C_{15}H_{15}N_3O_2$) of 100% purity and molecular weight 269.31g/mol, HCl (hydrochloric Acid) of 37% purity, density 1.19 and molecular weight 36.5g/mol and NaOH (Sodium Hydroxide) of 98% purity and molecular weight 40g/mol. The biological material was composed of cocoa pod shells of the Forastero type.

2.2. Methods

2.2.1. Method for the preparation of coals

The preparation of this coal was carried out in a single step: carbonization.. A mass of crushed pod shells and distilled water was introduced into a 250ml beaker. The mixture was stirred for a while. After homogenization, the mixture was introduced into a mitten oven. The final carbonization temperature was 400°C with a temperature gradient of 10°C/min and insulated bearing of 3 hours. The resulting coal was washed abundantly with distilled water and dried in oven at 105°C for 24 hours. The coal was packaged in a glass jar until it was used.

2.2.2. Preparation of solutions

The methyl red solution was prepared by dissolving a certain mass with distilled water in a 1 L flask. Methyl red has a molecular weight of 269.31 g/mol. The concentrations of the solution were determined by a UV-Visible spectrophotometer of the Hach DR 1900 type. The residual concentration of methyl red is measured at the wavelength λ=523 nm.

2.2.3. Kinetic study of methyl red adsorption: equilibrium time and quantity adsorbed

The principle was to follow the elimination of methyl red by coal over time according to the protocol below: 50mL of the methyl red solution of concentration 17mg/L and 0.05g of coal were putted in beaker. The mixture was put under magnetic stirring

at predefined times. The residual concentration (Cr) was determined using the calibration curve equation. The quantity of dye absorbed over the time of the experiments was determined by Eq. (1):

$$qt = (C_0 - C_t) * V / m \quad (1)$$

where: C_0 is initial dye concentration (mg/L), Ct is residual dye concentration at time t, V is volume of solution (L) and m is mass of adsorbent used (g) (Beekaroo and Mudhoo, 2011), qt: Quantity of dye adsorbed (mg/g).

2.2.4. Study of some adsorption parameters

- *Influence of the quantity of adsorbate material*

The volume of the dye solution (17 mg/L, pH=5.30) had been varied from : 20mL; 50mL; 70mL; 100mL; 150mL; 200mL; 300mL; 400mL; 500mL. In a methyl red solution of concentration 17 mg/L and pH=5.30, a mass of 0.05g of coal was introduced. The mixture was stirred for 40 min.

- *Effect of the pH of the methyl red solution*

The pH was essential in the study of adsorption phenomena. The potential of surface charges of the adsorbent changes the behaviour of the adsorbate (degree of ionisation). The interaction mechanism between the adsorbate (methyl red) and the adsorbent used (coal) changes according to the pH of the solution (Goudarzi et al., 2008; Mane et al., 2007). The pH of the solution with a concentration of 17mg/L and a volume of 50 mL is adjusted with 0.1M hydrochloric acid and 0.1M sodium hydroxide solutions.

2.2.5. Modelling of adsorption kinetics

- *Pseudo-first-order model*

In this model, the adsorption rate at time t is proportional to the difference between the quantity adsorbed at equilibrium qe and the quantity qt adsorbed at that time (Ouali et al., 2015). With this model given by the (Eq. 2), adsorption is reversible (Akkouche and Amouchas, 2017, Muthanna et al., 2012; Ouali et al., 2015).

$$\frac{dqt}{dt} = K_1(q_e - q_t) \quad (2)$$

The integration of (Eq. 2) for t from 0 to t and qt from 0 to qt gives the (Eq. 3):

$$\ln(q_e - q_t) = \ln qe - K_1 t \quad (3)$$

where: qe - quantity of solute adsorbed at time t (mg/g); qt - quantity of solute adsorbed at time t (mg/g); K_1 – rate constant (min^{-1}) of the pseudo first-order equation determined by plotting; ln (qe-qt) as a function of time (t) (Beekaroo and Mudhoo, 2011).

- *Pseudo-second order model*

According to Ho et al. (2000), the kinetic model of the pseudo second order was expressed by Eq. (4):

$$\frac{dqt}{dt} = K_2(q_e - q_t)^2 \quad (4)$$

The integration of Eq. (4) for t from 0 to t and qt from 0 to qt gives the (Eq. 5):

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

The kinetic parameters of the model, including the Adsorption Rate Constant K_2 ($g.mg^{-1}.min^{-1}$) and the equilibrium adsorption capacity q_e ($mg.\ g^{-1}$) (Ademiluyi and Abidde, 2016) by plotting the line: $t/q_t = f(t)$ where: $1/q_e$ was the slope and $1/K_2 q_e^2$ the intercept at the origin of this line. This model suggests the existence of chemisorption, an exchange of electrons between the adsorbate molecules and the solid adsorbent. (Hamoudi et al., 2018; Khalfaoui, 2012; Pisarev, 2012).

- *Intra-particle diffusion model*

The intraparticle diffusion model is based on the solution of Fick's second diffusion law, which is approximated for short times (Obradovic, 2020). The intraparticle scattering model is generally applied to experimental data in a simplified form (Eq. 6) (Obradovic, 2020):

$$q_e = K_d * t^{1/2} \quad (6)$$

with Kd: Intra-particle diffusion rate constant ($mg/g.min^{1/2}$).

- *Elovich kinetic model*

Elovich's equation is expressed by the (Eq. 7) (Low, 1960):

$$\frac{dqt}{dt} = \alpha.\exp(-\beta q_t) \quad (7)$$

where qt is the sorption capacity at time t (mg g-1), α is the initial sorption rate ($mg\ g^{-1}\ min^{-1}$) and β is the desorption constant (g mg-1) (Kandisa et al., 2018).

The integration of Eq. (7) using the following boundary conditions: q_0 =0 to t=0 and q_t=q_t to t=t, and with $\alpha.\beta\ t >> 1$, gives us Eq. (7), called the linearized form of this model (Gautam and Chattopadhyaya, 2016):

$$q_t = \frac{1}{\beta}\ln(\alpha.\beta) + \frac{1}{\beta}\ln t \quad (8)$$

Eq. (8) was used to simulate the experimental data by plotting q_t versus ln(t) curve.

2.2.6. Modelling of the adsorption isotherm

- *Langmuir isothermal model*

The widely used model is based on reactionary assumptions. The solid is assumed to have a limited adsorption capacity q_m related to a limited number of adsorption sites (monomolecular layer) (Kumar et al.,

2010; Sivashankar et al., 2014). This is given by Eq. (9):

$$\frac{qe}{qm} = \theta = \frac{K_L C_e}{(1 + K_L C_e)} \quad (9)$$

where: θ: recovery rate.

The linear form of the Langmuir isotherm is given by (Eq. 10):

$$\frac{Ce}{qe} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (10)$$

where: q_m is the maximum adsorption capacity of adsorbent ($mg.g^{-1}$) and K_L refers to the Langmuir constant related to the adsorption capacity and adsorption rate. In addition, a dimensionless constant separation factor (R_L) was employed to determine whether the adsorption is favorable or unfavorable as follows (Eq. 11):

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (11)$$

where: C_0 is the initial concentration (mg. L^{-1}) and K_L is the Langmuir constant. The value of R_L indicated that the adsorption was unfavorable (R_L >1), favorable (0< R_L <1), or unfavourable (R_L =1) (Wan et al., 2016).

- *Freundlich isothermal model*

This model describes adsorption on heterogeneous surfaces (Kumar et al., 2010; Sivashankar et al., 2014). It is given by the (Eq. 12):

$$q_e = k_F C_e^{\frac{1}{n}} \quad (12)$$

From the logarithmic function, we obtain the following linear form (Eq. 13):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (13)$$

with k_F(l.kg-1) and n (dimensionless) of the experimental constants.

The graph describing ln(q_e) as a function of ln(Ce) gives a straight line of slope n, whose intercept at the origin is ln(k_F). According to Eq. (13), the isotherm has an infinite slope at the origin and does not have a strict saturation plateau. The parameter n in the Freundlich equation is an indicator of the affinity and capacity of each coal/pollutant pair: for n > 1, adsorption is quantitatively greater and for n < 1 it is lower (Reffas, 2010).

- *Elovich isothermal model*

Elovich's model (Akolo and Kovo, 2015) describes multi-layer adsorption by the Eq. (14):

$$\theta = q_e / q_m = k_E \cdot C_e \cdot \exp(q_e / q_m) \quad (14)$$

The action of the logarithmic function on Eq. (14) results in the following linearized form (Eq. 15):

$$\ln(q_e / C_e) = \ln(k_E \cdot q_m) - \frac{q_e}{q_m} \quad (15)$$

where: q_m (mg/g): the maximum adsorbed capacity per unit mass of adsorbent; q_e (mg/g): equilibrium adsorption capacity; k_E (L/mg): Elovich's equilibrium constant C_e (mg/L): the equilibrium concentration of the adsorbate.

If Elovich's relation is verified, the plot of the curve: ln(q_e/q_m) = f(q_e), gives us a straight line of slope a=-1/qm, and of intercept at the origin equal to ln($k_E.q_m$).

3. Results and discussion

3.1. Adsorption kinetics

Fig. 1 shows the adsorption kinetics of methyl red on coal. The methyl red adsorption kinetics (Fig. 1) have three distinct phases. A first phase of rapid adsorption ranging from 0 to 20 minutes. A second phase of slow adsorption between 20 and 40 minutes. A third adsorption phase with a plateau between 40 and 80 minutes. The first adsorption phase is explained by the faster and larger occupation of the numerous vacant active sites available on the surface of the coals (Dincer et al., 2007). The second phase of adsorption corresponds to the diffusion of adsorbates (methyl red) to less accessible sites. This slows down the adsorption rate before reaching equilibrium (Khalfaoui, 2012). The third adsorption phase indicates the uniformity of the quantity of methyl red adsorbed over a period of 40 to 80 minutes. Thus, the adsorption equilibrium of the methyl red dye on the charcoal was reached after 40 minutes of stirring.

With a maximum adsorption capacity of 12.232 mg/g of methyl red on coal. Thus, at equilibrium, 71.95% of the initial quantity of methyl red has been removed. By studying the adsorption of the same dye on the SB-sebacoyl material, Rechache (2019) determined an equilibrium time of 10 minutes. This is less than four times the time it takes for the dye to reach equilibrium on coal. And this time resulted in a methyl red adsorption rate of 51.92%. This value is lower than that recorded with coal. However, this superiority could be related to the initial concentration of methyl red. In fact, the initial concentration of the solutions were respectively 100 mg/L for Rechache (2019) and 17 mg/L in this study.

This quantity adsorbed of an acid dye on a coal, especially coal, seems quite considerable in the light of other studies. For example, we note for acid dyes: Bemacid Yellow and Bemacid Blue on activated coals from date pedicels, pomegranate peel, Thomson peel and clementine peel for very long equilibrium times of very low adsorbed quantities. For Bemacid Yellow, at equilibrium, the quantities of dye adsorbed are in the following order: 1.64 mg/g (date pedicels)> 1.01 mg/g (pomegranate peel)> 0.50 mg/g (Thomson peel) > 0.38 mg/g (clementine peel) for an initial concentration of 100 mg/L (Benaissa, 2012). However, the high initial concentration during their study could explain the low quantities adsorbed.

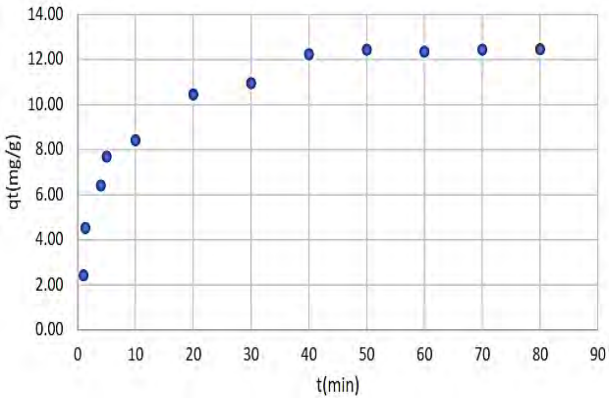

Fig. 1. Evolution of the quantity of methyl red adsorbed by the coal as a function of contact time at C_0=17mg/L, pH=5.30 and ambient temperature 20°C

3.2. Influence of some adsorption parameters

Figs. 2-3 show the influences of the quantity of material and the pH of the aqueous solution on the adsorption of the methyl red dye. The result on the influence of the material quantity show that the maximum adsorption capacity of methyl red dye increases with the increase in the material quantity. Indeed, when quantity of material was changed from 0.002 moles to 0.018 moles, the equilibrium adsorption increased from 7.536 to 27.544 mg/g. This behavior could be attributed to the fact that as material quantity is increasing, more dye is made available for adsorption on the adsorbent.

Although this study is different from the one conducted very often by many scientists (Aarfane et al., 2014; Faouzia, 2014; Jawad and Abdulhameed, 2020a) where the concentration of the solution was varied. This result, however, could be attributed to the high concentration gradient, which provided a driving force to move the methyl red dye molecules to active adsorption sites (Jawad and Abdulhameed, 2020a). The significant value of the correlation coefficient (R^2=0.9991) indicates a good correlation between the maximum adsorption capacity and the initial material quantity. In addition, there is no saturation of the active sites of the adsorbent due to the increase in the quantities of solute adsorbed.

The variation of the pH of the solution on the adsorption of methyl red (Fig. 3) shows an increase in the adsorption of acidic to basic pH. In fact, when pH was changed from 3.56 to 10, the equilibrium adsorption increased from 6.39 to 13.88 mg/g level. However, as methyl red is an anionic acid dye, the maximum adsorption capacity should decrease from acidic to basic pH. Indeed, according to some authors, when the pH value is low, the surface of the coals would be surrounded by H^+ ions which decreases the interaction of ions from cationic pollutants or increases the interaction of ions from anionic pollutants with the sites of activated coals. On the other hand, at high pH values, the concentration of H^+ decreases which leads to a good interaction between ions from cationic pollutants or a poor interaction of ions from anionic pollutants and the surface sites (Daimei et al., 2011; Faouzia, 2014; Houas et al., 1999; Murat et al., 2014; Sakr et al., 2014; Zohra et al., 2008).

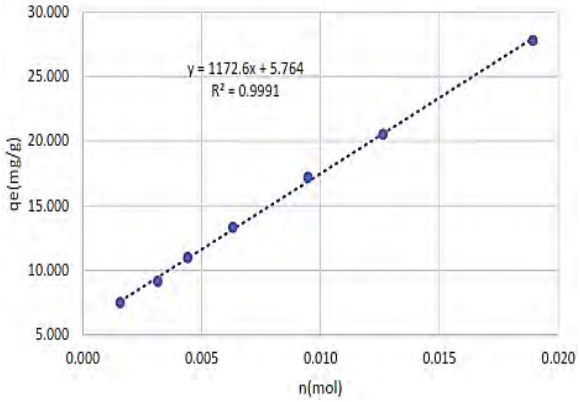

Fig. 2. Evolution of the adsorbed quantity of methyl red on coal (C=17mg/L, t=40min, pH=5.30 and T=20°C)

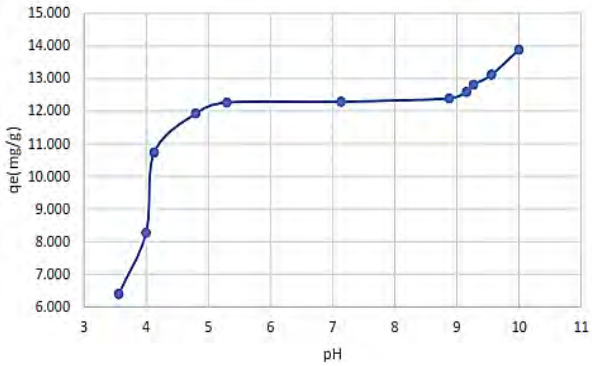

Fig. 3. Evolution of the quantity of methyl red adsorbed on coal as a function of pH

However, these results are similar to the results observed by Kra et al. (2015) and Kouadio et al. (2019) in their work on the removal of methylene blue in aqueous solution by activated coals based on two varieties of Acacia (auriculiformis and mangium) and cocoa pod shell. The results show that as the pH increases, the surface area of the adsorbent would favour a greater adsorption of the methyl red molecule. As for Rechache (2019), he found that the rate of elimination of methyl red by the SB-sebacoyl material remains constant from pH=1 to pH=13. Thus, the pH of the solution has no influence on the removal of this dye by the SB-sebacoyl material.

3.3. Application of kinetic models to the experimental results of the adsorption of methyl red by coal

Graphs of the equations of the different kinetic models of the adsorption of the methyl red dye are given in Fig. 4. The calculated constants are grouped in Table 1. As shown in Fig. 4 and Table 1, the pseudo second order kinetic model gave a higher correlation coefficient R^2 than the pseudo first order, the intra particle diffusion and Elovich kinetics models.

Fig. 4c shows two straight lines from the function qt = f ($t_{0.5}$). Neither line passes through the

origin of the graph (Fig. 4c). The diffusion of the methyl red dye into the pores of the coal is therefore not the only factor limiting the adsorption kinetics. When intra-particle diffusion is the only step limiting the speed of the whole adsorption process, the qt versus $t_{0.5}$ curve passes through the origin. The observed double linearity implies the existence of two steps (Ademiluyi and Abidde, 2016):

- the rapid transfer of methyl red from the solution and through the liquid film to the surface of the coal (Bhaumik et al, 2016).
- the slow diffusion of methyl red into the pores of the coal, characterizing the intra-particle diffusion during the adsorption process (Bhaumik et al, 2016).

According to Fayoud et al. (2015) the dye is first adsorbed by the outer surface so that the adsorption rate is very high. Once the outer surface is completely saturated, the dye molecule diffuses into the internal pores within the particles, and is finally adsorbed by the inner surface of the adsorbent. As the dye molecules diffuse through the internal pores or along the surface wall of the pores in the particles, the diffusion resistance increases, resulting in a decrease in the diffusion rate.

According to Fig. 4d and Table 1, a correlation coefficient of 0.9767 is observed with Elovich's kinetic model. This value would indicate the existence of chemical interactions between the anionic form of methyl red and the functional groups of the coal. The experimental maximum adsorption capacity (qexp) obtained in this study (400°C) is almost equal to that obtained (12.36 mg/g) by Kouadio et al. (2019) with carbonised coal at 450°C.

3.4. Application of adsorption isotherms to the mechanism of adsorption of methyl red by coal

Graphs of the isotherms of the adsorption of the methyl red dye are given in Fig. 5. The isothermal constants are listed in Table 2. The application of Langmuir model to the adsorption of methyl red on coal (Fig. 5) gives R2, q_{max} and K_L equal to 0.9937, 5.64 mg.g-1 and 0.266 L.mg-1 respectively (Table 2). With the Freundlich model (Fig. 5b), R^2, K_F and 1/n are 0.8907, 117.402 L/mg and 1.08, respectively (Table 2). For the Elovich isotherm (Fig. 5c), R^2, K_E and q_{max} are 0.8941, 0.039 L/mg and 8.873 mg/g, respectively (Table 2).

These different results show that the Langmuir isothermal linear model is best for describing the adsorption of the methyl red dye on coal. This adsorption of methyl red on coal would be carried out as a monolayer on energy homogeneous adsorption sites and without interaction between the adsorbed cations of the dye (Benhafsa et al., 2018). As for Rechache's work (2019), it showed that Freundlich's model perfectly describes the removal of methyl red by the SB-Sebacoyl material.

4. Conclusions

This study is part of both the environmental remediation and the development of agricultural waste. Its main objective is to experimentally study the adsorption of methyl red on coal from cocoa pod shells. The study was carried out in three different ways:

Table 1. Parameters of methyl red adsorption kinetics on coal

Pseudo-first order kinetics			
q_{exp} (mg/g)	k_1(min^{-1})	$q_{e\ cal}$ (mg/g)	R^2
12.232	0.066	7.810	0.9384
Pseudo-second order kinetics			
q_{exp} (mg/g)	k_1(g/mg.min^{-1})	$q_{e\ cal}$ (mg/g)	R^2
12.232	0.018	13.175	0.9986
Intra-particle diffusion kinetics			
q_{exp} (mg/g)	k_d(g/mg.min$^{1/2}$)	$q_{e\ cal}$ (mg/g)	R^2
12.232	0.018	13.175	0.9986
Elovich kinetics			
q_{exp} (mg/g)	β(g/mg)	α(mg/g.min)	R^2
12.232	0.455	10.966	0.9767

Table 2. Parameters of the methyl red adsorption isotherm on coal

Models	***Parameters***	***Values***
Langmuir	R^2	0.9937
	q_{max}(mg/g)	5.640
	K_L(L/mg)	0.266
Freundlich	R^2	0.8907
	K_F(L/mg)	117.402
	1/n	1.083
	N	0.924
Elovich	R^2	0.8941
	q_m (mg/g)	8.873
	k_E (L/mg)	0.039

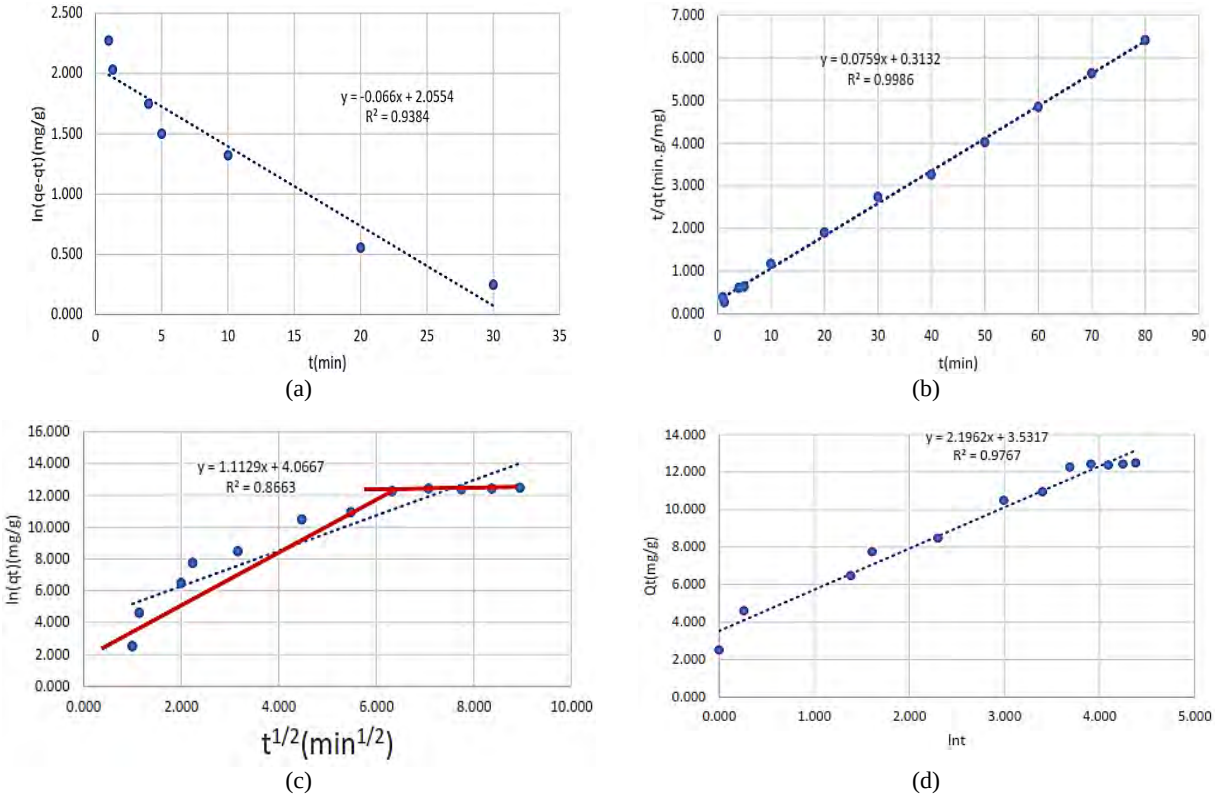

Fig. 4. Models of the kinetics of the adsorption of the methyl red dye on coal; (a) Pseudo-first order model of methyl red adsorption on coal; (b) Pseudo-second order model of methyl red adsorption on coal; (c) Methyl red adsorption intra-particle scattering model of methyl red adsorption on coal;(d) Elovich kinetic model of methyl red adsorption on coal

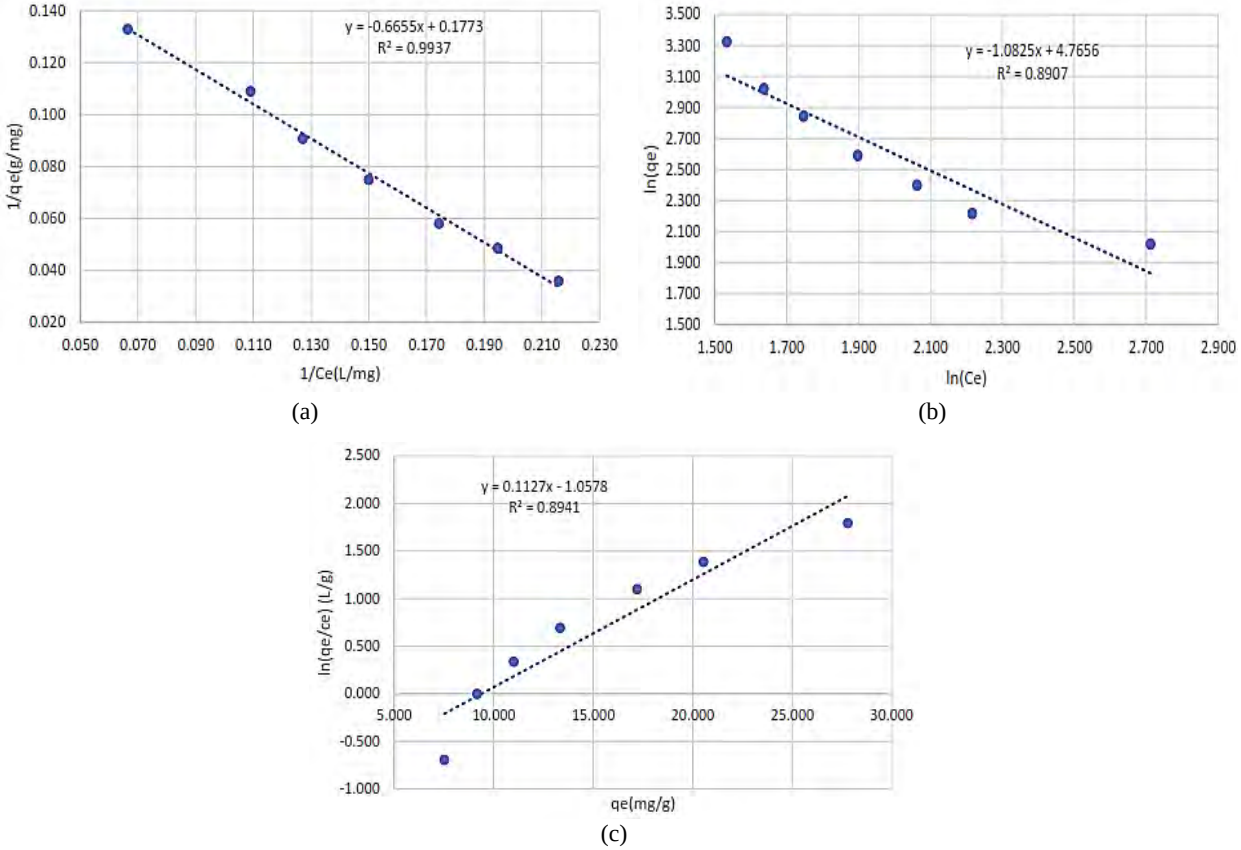

Fig. 5. Models of isotherms for methyl red dye adsorption on coal: (a) Langmuir isothermal linear model to the adsorption of methyl red on coal; (b) Freundlich isothermal linear model to the adsorption of methyl red on coal; (c) Elovich isothermal linear model to the adsorption of methyl red on coal

- study of some adsorption parameters.
- application of kinetic models to the experimental results of the adsorption of methyl red by coal,
-application of adsorption isotherms to the mechanism of adsorption of methyl red by coal.

From this study, we retain that:

- the adsorption kinetics of the methyl red dye (anionic acid) on coal leads to an equilibrium time of 40 min and an equilibrium calculated adsorbed quantity of 12.232 mg/g.
- the quantity of methyl red adsorbed increases from acidic to basic pH
- the adsorption capacity of the methyl red dye is also influenced by the quantity of initial adsorption. As the quantity of initial material is increased, the quantity of adsorbed material increases.
- the kinetics of elimination of the methyl red dye by the coal in solution follows a pseudo-second order kinetics with correlation coefficients higher than 0.9986.
- the study of the phenomenon of adsorption of the methyl red dye by the coal shows that the elimination follows the Langmuir model with a correlation coefficient greater than 0.9937.

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