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Design and application of sintered clay pellets for the removal of methylene blue

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Abstract

Industries use synthetic dyes and toxic organic compounds that pollute these waste waters, sometimes with significant fluxes. This work deals with the study of the elimination of methylene blue dye by sintered pellets based on alluvial clay. The pellet formulation was made with a proportion between the amount of the dry material and the amount of 90g/20mL distilled water, followed by a heat treatment of the pellets (100 °C to 500 °C). The adsorption tests showed that equilibrium was established after 25 minutes with 0.086 mg/g and 0.096 mg/g of MB removed by the pellets at 500 °C and 400 °C. The maximum percentage of adsorption of the pellets at 500°C is 67% that of the pellets at 400 °C is 70%. The adsorption of the methylene blue dye on the sintered pellets is described by pseudo-second-order kinetics. Thermodynamic parameters have shown that MB adsorption is less favored, exothermic and of a physical nature. Adequate MB adsorption temperature is 313K. The study of adsorption by pellets is rapid at low MB concentrations with 0.097 mg/g and 0.109 mg/g MB removed at 400 °C and 500 °C. The correct pH for the elimination of MB is 6.6. The Langmuir model expresses better the elimination of MB by pellets at 500 °C ($R^2 = 0.962$), while that of Dubinin-Radushkevich better expresses the elimination of MB at 400 °C ($R^2 = 0.996$). The pellets at 400 °C and 500 °C are stable in solution and show a good adsorption capacity for methylene blue.

Keywords: pollution control; clay dumpling; waste; methylene blue

Introduction

The pollution of water and soil, accidentally or deliberately by some industrial (hydrocarbons, phenols, dyes,) or agricultural (pesticides, fertilizers,) chemicals, has become a major problem and concern, since it is a source of environmental degradation and is of particular interest at the international level (Omar, 2003) [19]. Methylene blue is the dye most commonly used in dyeing cotton, wood and silk. It can cause eye burns that cause permanent injuries to humans and animals. Inhalation can lead to breathing difficulties and ingestion through the mouth produces a burning sensation, nausea, vomiting, sweating and heavy cold sweats (Asmaa *et al.*, 2010, Domga *et al.*, 2015) [4, 8]. The treatment of industrial waste containing this type of dye is of great interest.

Different techniques have been used for the removal of these soluble pollutants in industrial or domestic effluents. They are different from each other and can be cited by way of illustration adsorption, flotation, precipitation, ion exchange, liquid-liquid extraction, membrane filtration, electrocoagulation etc (Khalifaoui, 2012) [16]. Adsorption is one of the most adopted techniques for this removal of pollutants, because of its great ability to purify contaminated water (Domga *et al.*, 2016) [9]. Activated carbon is the most commonly used adsorbent but remains very expensive and also requires regeneration as a limiting factor (Adjia *et al.*, 2012a) [1]. This has therefore encouraged research by orienting them towards treatment processes using natural materials (clays) which are less expensive and widely available (Djoufac *et al.*, 2007, Nguetnkam *et al.*, 2007) [7, 18]. Clays play a significant role in a wide range of environmental problems and applications are constantly increasing (Ghazala, 2009) [12]. Indeed, several previous works have been carried out for the adsorption of vegetable oil dyes (Kamga *et al.*, 2000, Bike *et al.*, 2005) [15, 6], anionic and cationic dyes (Baliti *et al.*, 2014, Sadki *et al.*, 2014) [5, 21], and heavy metals solutions (Adjia *et al.*, 2012b) [2]. The Far North region of Cameroon is known for its vast clay deposits. In particular, the

clays of the family of film and chromic vertisols may contain certain swelling clays of type 2: 1, with high retention capacities, which are mainly used in the building materials, and cement and ceramic production industries (Nguetnkam *et al.*, 2007; Adjia *et al.*, 2012) [18], and also in the treatment of industrial effluents. However, in the regions of the Adamaoua, the Far North, and North Cameroon, artisanal populations are shaping the canaries based on alluvial clay for water purification. To do this, they consolidate their canaries by performing a thermal cooking. It is with this in mind that we propose to formulate sintered pellets based on clay in order to get closer to the artisanal populations. In addition, the research component of this work is to overcome the problem of simple filtration, requiring a lot of time during laboratory manipulations. Hence also the idea of designing clay pellets (Adjia, 2012). The aim of this study is to exploit the potential and the retention capacity of alluvial clay sintered pellets from the Far North region in water depollution to remove methylene blue (MB). The general objective of the work is to eliminate the methylene blue by the sintered pellets based on alluvial clays from the Far North of Cameroon.

Material and Methods

The material used in this work consists essentially of sintered clay pellets and methylene blue (Fluka 96%) prepared in the laboratory.

Sampling

The sampling site is the bed of a dried mayo of the dry tropical zone of Cameroon, located near the town of Maroua (between Kaélé and Maroua). Its Global Positioning System (GPS) coordinates are 10°02'883N and 014°23.084E.

Sampling procedure

With the technical support of the research team's geologists, the sampling area was determined and different sampling points were located using a GPS-based portable satellite positioning system (Adjia *et al.*, 2012). Clay samples were taken randomly. Three samples of the surface layer (about 20 cm deep) were made at one meter intervals using a stainless steel scoop while repeating the operation 5 times in "star" around a central point to obtain a representative sample of the sampling area. In the field, the clay samples are kept cold in a cooler with cold packs. The polythene bags containing the samples are then placed at 4°C in a refrigerator as quickly as possible.

Splitting

The clay samples taken are placed in high density polyethylene bags and transported to the laboratory. They were then crushed with an artisanal crusher, and manually crushed and dried at room temperature in the laboratory for about 72 hours. After homogenization (pre-soaking with distilled water), the fractions are collected by quartering for the various analyzes. "Quartering" makes it possible to share the crushed and homogenized dry material in several identical parts, using a suitable device, so that each part is as representative as possible of the overall material.

Fraction of 50µm and fraction of 200µm

This separation allowed us to obtain fractions whose particle sizes are respectively less than 50 and 200µm. Here sieves were used whose grids are made of polyethylene. For this

purpose, 3000 g of powder obtained after grinding are pre-soaked in distilled water for 24 hours. The mixture is then homogenized and then placed in an ultrasound tank of ELMA TRANSSONIC T310 type of frequency 50 KHz for 20 minutes. After dispersion, the mixture is sieved using a 50µm mesh polyethylene sieve to obtain the 50µm clay fraction; or a polyethylene sieve with 200µm mesh to obtain the 200µm fraction. Particles of unwanted size are retained by the sieve. The resulting mixture is dried at 105°C until completely evaporated and sprayed into an Agathe mortar. In the framework of this study, therefore, fractions of different sizes are obtained, in particular fraction <50µm and fraction <200µm (50µm technological purpose and 200µm extension purpose). The clay sample was oxidized with oxygenated water (H₂O₂) to remove organic matter prior to fractionation. Thus, only one type of granular separation was performed on the sample: wet sieving separation.

Clay balls design

The design of the pellets follows the following steps:

- 90 g of natural clay powder were introduced into a polyethylene container, then mixed and homogenized with distilled water (20 ml);
- Next, clay balls are formed, while respecting a size of about 1 cm in diameter measured using the sliding stone and 1 g in weight (the pellets have a spherical shape);
- Finally, after brief baking (direct mode) for 10 minutes in the oven, at temperatures of 100 °C, 200 °C, 300 °C, 400 °C and 500 °C, the clay balls have lost any their free water and are removed from the oven.

In addition, the adsorption test of the pellets in distilled water for 48 h, the mechanical strength and the capacity of the adsorbing pellets MB were the criteria that were evaluated to determine if the shaping of the adsorbent is appropriate for the desired use. Some natural clay pellets were sun-dried for two whole days. The objective sought here is to determine the pellets which are stable in solution.

Thermal treatment of pellets

The oven used is a monobloc oven. The samples are introduced into the various crucibles according to the temperature steps (100 °C to 500 °C) and pushed to the center of the oven by means of a rod and these are removed from the oven after a 10 minute cooking. In this work, we used the direct cooking mode.

Preparation of the stock solution and desired concentration solutions

To do this, we prepare a mother solution of MB 5mg/L concentration which will then be diluted by a calibration range of 0.8, 1.6, 2.4, 3.2, 4 and 5mg/L MB in steps of 2 in order to plot the calibration line. The reading of the optical density was made at a maximum wavelength of 664 nm. These dilutions correspond to the minimum and maximum levels of MB in wastewater according to the standards in force.

Preparation of polluting solutions for adsorption

The adsorption experiments were performed at different initial values of pH, temperature, and initial dye concentration. The tests were performed by immersing a sintered pellet in 25 mL of the synthetic methylene blue dye solution at 5 mg/L. The pH of the MB solution is adjusted

using 6N sulfuric acid or 0.5N sodium hydroxide. Then recovery of the supernatant and the absorbance of the supernatant was measured using a UV/visible spectrometer of GENESYS 10S type at the wavelength which corresponds to the maximum absorbance of the MB solution ($\lambda_{max}=664\text{nm}$). The residual dye concentration was determined using the calibration curve performed with a range of known MB concentrations (Harouna *et al.*, 2015) [8, 13].

The adsorption capacity of the methylene blue dye by the sintered pellets was calculated using the following formula:

$$q_e = (C_0 - C_e) \frac{V}{m_{\text{adsorbant}}} \quad (\text{mg/g}) \quad (1)$$

With: V is the volume of adsorbate (L);
M the mass of the pellet (g);

C_0 and C_e (mg/L) are the initial concentration of MB and the concentration of MB at the moment, respectively.

Phenomenon of adsorption of BM by sintered pellets (adsorption test)

The purpose of this experiment is to determine from what cooking temperature the pellets acquire water-resistant cohesion to choose the pellets that are stable in solution.

Operating mode

The procedure is very simple. It only involves immersing the pellets in containers containing distilled water for 48 hours and observing whether they are disintegrating or not, and if so after how long.

Modeling of MB adsorption kinetics

The adsorption kinetics of methylene blue by sintered pellets was studied using the pseudo-first-order, pseudo-second-order and intraparticle diffusion equations.

Kinetic model of pseudo-first order

The velocity equation of the pseudo-first-order kinetic model is given by the relation

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

Where q_e and q_t are respectively the relative amounts of adsorbed adsorption MB and at time t , k_1 (min^{-1}) is the pseudo-first order rate constant. Representing the $\log(q_e - q_t) = f(t)$ function, we obtain a straight line of slope $-\frac{k_1}{2.303}$ and an intercept of $\log q_e$ (Reddy *et al.*, 2010, Harouna *et al.*, 2015) [20, 8, 13].

Kinetic model of pseudo-second order

The pseudo-second-order kinetic model can be represented in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where q_e and q_t are respectively the relative quantities of MB adsorbed at equilibrium and at time t , k_2 is the pseudo-second-order rate constant. The adsorption of MB by the sintered pellets will follow the kinetic model of pseudo-second order if the correlation coefficient of the linear

regression of $\frac{t}{q} = f(t)$ is greater than 0.90 (Harouna *et al.*, 2015) [8, 13].

Kinetic model of intra particle diffusion

The intraparticle diffusion model can be represented by the equation:

$$q_t = k_{int} \sqrt{t} + C \quad (4)$$

Where q_t is the relative amount of adsorbed MB at time t , k_{int} is the intraparticle diffusion constant and C is a constant (Reddy *et al.*, 2010, Harouna *et al.*, 2015) [20, 8, 13]. The regression of the function $q_t = f(\sqrt{t})$, makes it possible to obtain a line of slope k_{int} and ordinate at the origin C .

Modeling of MB adsorption isotherms

The adsorption capacity was determined using the isotherms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich.

Langmuir model

The theory proposed by Langmuir is based on a homogeneous distribution of the adsorption sites. The Langmuir isotherm can be represented by the equation:

$$q_e = \frac{a K_L C_e}{1 + K_L C_e} \quad (5)$$

Where C_e is the residual relative amount of the MB at the adsorption equilibrium, q_e the relative amount of the adsorbed MB per gram of adsorbent, has the adsorbed amount to the monolayer and K_L the equilibrium adsorption constant. The representation of $\frac{q_e}{C_e}$ as a function of C_e makes it possible to determine the coefficients a and K_L for the adsorption of MB in solution (Fayoud *et al.*, 2015; Domga *et al.*, 2015) [11, 8].

Freundlich model

The simple and empirical model of Freundlich is the second most commonly used model. It is considered that it applies to many cases, especially in the case of an adsorbent with a heterogeneous adsorption surface (energetically different adsorption sites).

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

The linear expression of the Freundlich equation (6) is obtained by taking the logarithm of the equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

Where K_F and n are the constants respectively reflecting the measurement of the adsorption capacity and the adsorbent-adsorbate affinity. The constant n gives an indication of the intensity of the adsorption. It is generally accepted that low values of n ($0.1 < n < 0.5$) are characteristic of good adsorption, while higher values show moderate ($0.5 < n < 1$) or low adsorption. ($n > 1$). The constant " n " is very often replaced by " $1/n$ " or heterogeneity factor (Fadi, 2008, Harouna *et al.*, 2015) [10, 8, 13].

Temkin model

Adsorption is characterized by a uniform distribution of adsorption energy up to a maximum of energy. The isotherm of Temkin is given by the relation:

$$q_e = B \ln A + B \ln X_e \quad (8)$$

Where $B = RT/b$ is the Temkin constant assimilable to the adsorption energy and expressed in $\text{J} \cdot \text{mol}^{-1}$, R is the perfect gas constant ($8.314 \cdot 10^{-3} \text{ KJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), A the isothermal constant of Temkin, and T the absolute temperature (Reddy *et al.*, 2010, Kalavathy and Lima, 2010) [20, 14].

Dubinin-Radushkevich model (D-R)

His micropore volume filling theory is based on the fact that the adsorption potential is variable and that the free adsorption enthalpy is related to the degree of pore filling (Harouna *et al.*, 2015) [8, 13]. The Dubinin-Radushkevich isotherm is given by the equation:

$$q_e = q_m \exp(-K \varepsilon^2) \quad (9)$$

The linear expression of equation (9) can be on the following form:

$$\ln q_e = \ln q_m - K \varepsilon^2 \quad (10)$$

where q_e is the amount of MB adsorbed at equilibrium, K is a constant related to the average free energy of adsorption, q_m is the theoretical capacity in micropores, ε is the potential of Polanyi, equal to $RT \ln(1 + 1/C_e)$. The values of q_m and K are determined by the plot of $\ln q_e$ according to ε^2 (Reddy *et al.*, 2010, Kalavathy and Lima, 2010) [20, 14].

Effects of physicochemical parameters on BM adsorption

Effect of contact time

To measure the influence of time, several flasks containing 25 mL of the initial concentration BM solution 5 mg/L were made. One pellet (1g) is immersed in the MB solution for different times (5 to 60 min) in steps of 5 minutes; at normal pH of the solution (6.6), and at room temperature. The aim here is to determine the equilibrium time between the adsorbent and the adsorbate.

Effect of BM concentration

To measure the influence of the concentration, several MB solutions at different concentrations, at normal pH, ambient temperature and a pellet of 1 g in mass were fixed. The work is carried out for a concentration range of MB fixed from 2 to 10 ppm in steps of 2.

Effect of temperature

To measure the influence of temperature, we will have seven temperatures between 20 °C and 60 °C, initial concentration (5 mg/L), a fixed pellet and at normal pH. Temperature has two major effects on the adsorption process.

pH effect

The work is carried out in a pH range of from 2 to 12 in steps of 2 to observe the difference of the amounts adsorbed in acidic and basic medium.

Results and Discussion

Pellets adsorption test in distilled water

It is apparent from picture 1 that sun-dried pellets and pellets cooked from 100 °C to 300 °C are destabilized by the action of water and also, they are not favorable for adsorption. The pellets cooked at 400 °C and 500 °C are stable in water and favorable for adsorption. In addition, when a pellet dries, under the effect of the heat treatment, the capillary shrinkage brings the clay sheets closer together and the capillarity forces increase thus ensuring the mechanical cohesion of the pellet in the air. If the pellet is immersed in water, the pressure of the water exerted on it under the probable action of the osmotic forces, due to the presence in the medium of cations compensating for the ion deficiency of the support, prevail. On the capillarity and the pellet rehydrates. The rehydration of the (osmotic) pellet tends to move these particles away from each other, thus making the capillary forces more attractive and the pellet dislocated. This has been observed in our experience. In addition, the rehydration of montmorillonite causes its swelling by hydration of interfoliar cations.

During sintering, the departure of the OH groups by radical reaction creates points of physical cohesion within the pellet. This cohesion is opposed to osmotic forces when the pellet is immersed in water. At the beginning of the dehydroxylation, the points of cohesion are too few to fight against the dislocation of the pellet, but this one is made in coarser particles. When the dehydroxylation is more thorough, the points of cohesion make it possible to maintain the whole pellet. In sum, after the adsorption test and in view of the results obtained, the pellets cooked at 400 °C and 500 °C were chosen and will be used as adsorbents for the remainder of our study.

Kinetic study

Figure 2 shows the adsorption kinetics of MB by sintered natural clay pellets.

The curve in figure 2 shows that the MB adsorption process on the pellets is decomposed into three stages: a very rapid plateau due to the availability of the adsorption sites; followed by a plateau of latency due to the decrease of the adsorption sites; and finally another stage where the adsorption almost no longer exists, by the presence of a spread with a saturation of the adsorbent sites. The equilibrium is reached at 25 minutes of contact with 0.086 mg/g and 0.096 mg/g of MB removed by the pellets at 500 °C and 400 °C.

Modeling of adsorption kinetics

Correlation coefficients R^2 , equilibrium adsorbed MB quantities, and rate constants of different kinetic models that were tested are shown in Table 1.

It can be seen from Table 1 that the pseudo-first-order and pseudo-second-order models are suitable for describing adsorption of MB by sintered pellets given the high R^2 coefficients obtained for these models. From the results obtained, it is noted that the pseudo-second-order model is the most reliable for determining the order of adsorption kinetics of the BM by the pellets having a correlation coefficient exceeding 99%, and the values calculated by the pseudo-second-order model is very close to that determined experimentally (0.0886 mg/g) by the pellets.

Table 1: Summary of the constants of the different kinetic models and coefficients of determination R² (Cf formula (2); (3) and (4)).

Pellets	Pseudo first order model			Pseudo second order model			Intraparticle model		
	Q _{e,cal} (mg/g)	K ₁ (min ⁻¹)	R ²	Q _{e,cal} (mg/g)	K ₂ (g.mg ⁻¹ .min ⁻¹)	R ²	C (m ² .S ⁻¹)	K _{int} (mg/g.min ^{0.5})	R ²
400°C	0.004	-0.023	0.951	0.090	-8.229	0.997	0.106	-0.002	0.972
500°C	0.024	0.092	0.936	0.088	19.365	0.997	0.069	0.004	0.410

Adsorption isotherms

The variations in the amount of adsorbed MB per gram of adsorbent (q_e) as a function of the equilibrium concentration (C_e) were determined and the results were modeled.

$$q_e = \frac{(C_i - C_e)V}{m}$$

Where C_i is the initial concentration of the MB solution, C_e is the concentration of the MB solution after adsorption, m the mass of the pellet used and V the volume of the MB solution.

Figure 3 shows the adsorption isotherms of MB on the sintered pellets respectively. Whatever the temperature level considered, the adsorption of MB is very strong at low residual concentration, which indicates a high affinity between the MB and the adsorbent. In addition, the curve shows that the amount adsorbed increases rapidly to a maximum amount of MB adsorption of the order of 0.135 mg/g and 0.138 mg/g for pellets fired at 500°C and 400°C. The experimental results were thus confronted with the

theoretical models of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (Table 2).

It can be seen from Table 2 that the R² coefficients for the 4 models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) are generally greater than 0.95 with the exception of the Freundlich and Temkin model for the 500°C pellets. This result indicates that the experimental data satisfy all four adsorption models except for the Freundlich model for the 500°C plateau with R² = 0.872. However, the Langmuir adsorption isotherm better expresses the adsorption of MB by the pellets at 500°C, while the Dubinin-Radushkevich isotherm better expresses the adsorption of MB by the pellets at 400°C. The value of the Freundlich model n constant for pellets of 400°C is between 0 and 0.5 indicating that the adsorption is considered good, whereas it is low in the case of 500°C pellets because the coefficient n is greater than 1. Thus, we can say that there is a good affinity between the clay-based pellets and the MB.

Table 2: Constants of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich for adsorption of BM by sintered pellets (Cf formula (5); (7); (8) and (10)).

Pellets	Langmuir isotherm			Freundlich isotherm		
	a (mg/g)	K _L (L/mg)	R ²	K _F (mg/g)	n	R ²
400°C	0,184	0,811	0,951	0,024	0,493	0,966
500°C	0,168	0,831	0,962	0,071	2,556	0,872

Pellets	Temkin isotherm			Dubinin-Radushkevich isotherm			
	B	A (L/g)	R ²	K	q _m (mg/g)	R ²	E _S (Kj/mol)
400°C	0,131	1,111	0,988	0,008	0,247	0,996	7,805
500°C	0,040	5,620	0,909	0,003	0,152	0,958	13,519

Effect of initial MB concentration on adsorption

Figure 4 shows the amount of MB adsorption as a function of the concentration of the solution.

This figure shows that the amounts of adsorbed MB are not equivalent for the two temperature levels. In comparison with pellets sintered at 400°C, the maximum adsorption capacity in the case of pellets of 500°C is of the order of 0.109 mg/g, whereas in the case of pellets sintered at 400°C is of the order of 0.097 mg/g. The two isotherms show a plateau indicating the saturation of the surface sites and therefore the formation of the monolayer (Talidi, 2006, Domga *et al.*, 2015) [22, 8].

Determination of thermodynamic parameters

The adsorbed relative amounts obtained at different temperatures were used to calculate important thermodynamic properties such as Gibbs free standard energy ΔG° (Kj.mol⁻¹), standard enthalpy (ΔH°) (Kj.mol⁻¹), and the standard entropy (ΔS°) (Kj.mol⁻¹.K⁻¹). Standard

enthalpy (ΔH°) and entropy (ΔS°) (12) values were determined from the Van't Hoff equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

The representation of ln K_d as a function of 1/T of the Van't Hoff equation is a line of slope ΔH°/R and origin ordered ΔS°/R.

As shown in Table 3, the standard enthalpy values of MB adsorption for all sintered pellets are negative which confirms that the adsorption process is exothermic. In our case, the enthalpy values are less than 80 KJ.mol⁻¹, which means that the adsorption of MB by the pellets is of a physical nature. The values of entropy ΔS are negative, which means that MB molecules are more organized at the solid/liquid interface than in the liquid phase for these systems (Varlikli *et al.*, 2009; Konicki *et al.*, 2013) [23, 17].

Table 3: Thermodynamic parameters of adsorption of MB by sintered pellets at different temperatures (Cf formula (11) and (12)).

T(K)	Pellets 400°C				T(K)	Pellets 500°C			
	ΔG° (Kj.mol ⁻¹)	ΔH° (Kj.mol ⁻¹)	ΔS°	R ²		ΔG°	ΔH°	ΔS°	R ²
313	4.581	-42.486	-0.150	0.990	313	3.720	-9.734	-0.043	1
323	5.964				318	3.935			
328	6.714				323	4.150			
333	7.464								

Effect of pH on BM adsorption

Figure 5 shows the adsorbed amount of MB as a function of pH. For this, we have represented the variations of the adsorbed quantity as a function of the pH of the medium, starting from an initial MB concentration of 5mg/L.

It emerges from the results obtained in figure 5 that the influence of the pH on the adsorption is decisive because the adsorption increases with the pH in an acidic medium with obtaining methylene red up to pH = 6.6 (initial pH of the MB solution) for the pellets at 500 °C and 400 °C. In addition, for the pellets at 400 °C, a pH jump at initial pH of the MB solution is observed. However, in basic medium, the adsorption of MB is particularly favored (formation of the base of methylene blue).

Comparative study of the adsorption percentage of MB by sintered pellets at 400 °C and 500 °C.

Figure 6 shows a comparative study of the adsorption percentage of natural clay pellets with different heat treatment between 400 °C and 500 °C. This analysis shows that sintered pellets at 400 °C better adsorb MB than sintered pellets at 500 °C. The percentage of the maximum adsorbed quantity is reached at 8 ppm, it is substantially equal to 70% for the pellets at 400°C and 67% for the pellets at 500 °C. This difference in efficiency may be due to diffusion phenomena during immersion of the sintered pellets in the MB solution. In addition, the increase in the sintering temperature probably gives a less connected porosity and thus less easy diffusion of the MB into the center of the pellet.

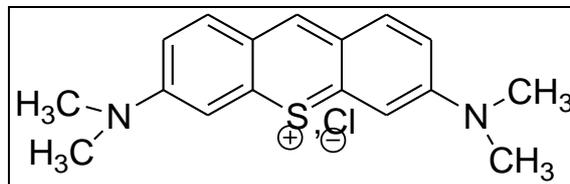


Fig 1: Structure of methylene blue

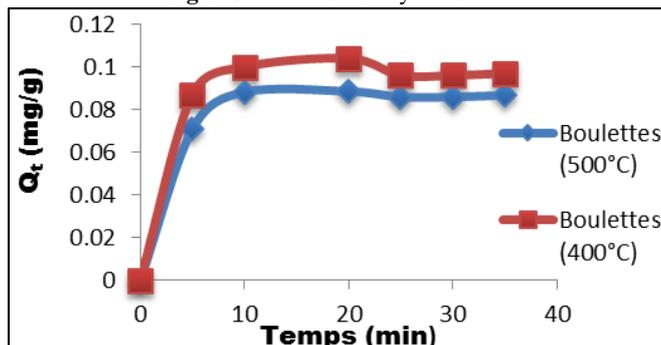


Fig 2: The kinetics of adsorption of MB by the sintered pellets

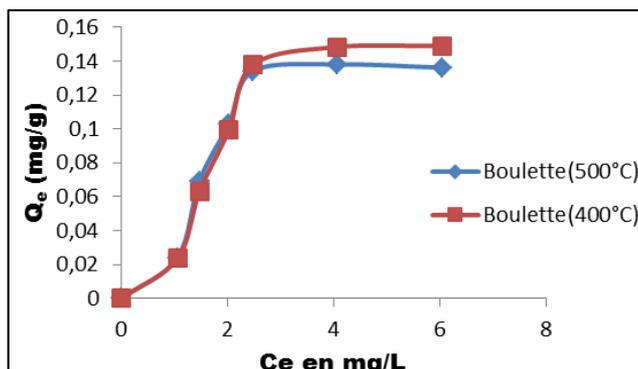


Fig 3: MB adsorption isotherm

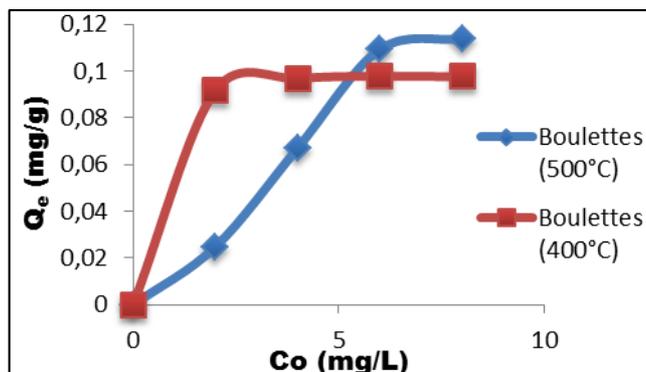
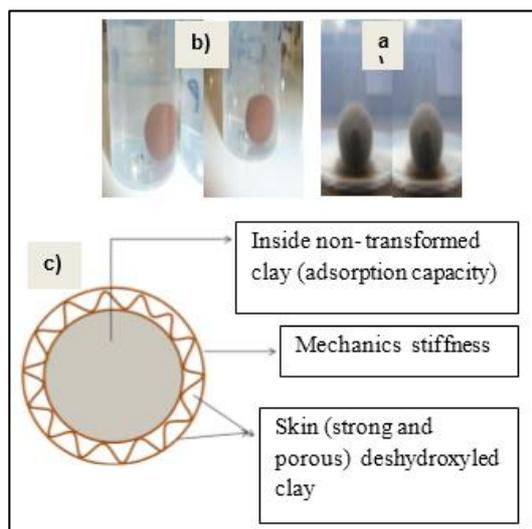


Fig 4: Influence of MB concentration on adsorption by sintered pellets; pH of the solution; mb = 1g; T = 298K; Contact time 25 min.



Picture 1: a) The sun-dried pellets and pellets cooked from 100 °C to 300 °C are destabilized in water, b) The pellets cooked at 400 °C and 500 °C are stable in water. c) The pellet’s sketch.

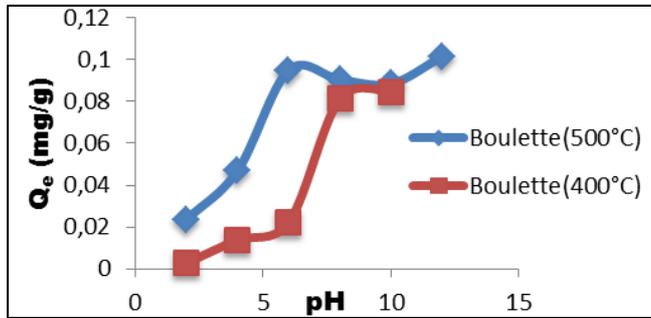


Fig 5: Influence of the pH on the adsorption of the MB by the sintered pellets; mb = 1g; Contact time 25 min; T = 298K.

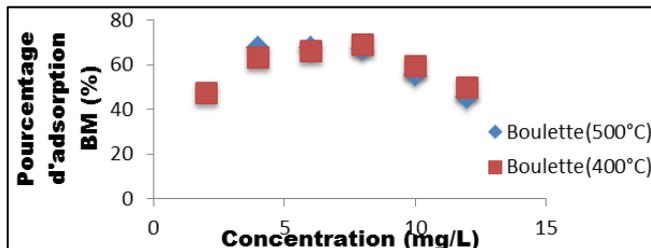


Fig 6: Comparative study of the percentage of adsorption of MB by sintered pellets at 400°C and 500°C.

Conclusion

The aim was to study the elimination of methylene blue by sintered pellets made from alluvial clay from the Far North of Cameroon. The study in particular of the influence of certain parameters (pH, concentrations, thermodynamic parameters, isotherms) on the adsorbent retention (MB) caught our attention. The essential work can be summarized in the following points:

The adsorption of MB by the sintered pellets at 400 °C and 500°C is rapid and the balance is reached at 25 minutes with 0.096 mg/g and 0.086 mg/g of adsorbed MB. The MB removal efficiencies by the pellets at 400 °C and 500 °C at this equilibrium are respectively 70% and 67%.

The pseudo-second-order kinetic model is applicable to the adsorption of MB, this implies on the assumption that the adsorption takes place in two phases: the diffusion of the adsorbate towards the surface of the adsorbent, followed by the adsorbent-adsorbate interaction.

The adsorption process is less favored, the MB adsorption reaction by the pellets is exothermic and the adsorption is of a physical type.

Our experimental results on MB adsorption were compared to the theoretical models of Langmuir, Freundlich, Temkin and Dubinin-radushkevich. The best correlation was obtained with the Langmuir, Freundlich, Dubinin-radushkevich and Temkin models for pellets sintered at 400°C; but more closely follows the Dubinin-radushkevich model ($R^2 = 0.996$) whereas the models that better describe MB adsorption by pellets at 500 °C are the Langmuir and Dubinin-radushkevich models; but better follows the Langmuir model ($R^2 = 0.962$). The value of the n Freundlich model constant for pellets at 400 °C is between 0 and 0.5 indicating that the adsorption is considered good, whereas it is low in the case of 500°C pellets because the coefficient n is greater than 1. The pellets obtained by thermal treatment of the clay at 400°C and 500°C are stable in solution and show a good adsorption capacity of the MB.

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