



# **Valorization of Green Clay from Bouaflé (Ivory Coast) in the Simultaneous Elimination of Organic Pollutants and Metallic Trace Elements by Adsorption: Case of Methylene Blue and Cadmium Ions**

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## **Authors' contributions**

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

## **Article Information**

DOI: 10.9734/CSJI/2020/v29i830199

### Editor(s):

(1) Dr. Francisco Marquez-Linares, Universidad Ana G. Méndez, USA.

### Reviewers:

(1) Flavia C. Zacconi, Pontificia Universidad Católica de Chile, Chile.

(2) Cláudia Cândida Silva, Universidade do Estado do Amazonas, Brazil.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/63793>

**Original Research Article**

**Received 08 October 2020**

**Accepted 12 December 2020**

**Published 31 December 2020**

## **ABSTRACT**

The objective of this work was to valorize the clays of Côte d'Ivoire in the treatment of wastewater. The study focused on the ability of raw clays from Bouaflé city to adsorb methylene blue and cadmium ions, in aqueous solution. The physicochemical characteristics of the clay were determined using the measurement of its specific surface area, chemical analysis and mineralogical analysis. It emerges from these characterizations that clay is essentially composed of

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type 2/1 minerals such as illite (32.94%), type 1/1 kaolinite (8.47%), quartz (40.23 %) and approximately iron oxy-hydroxides (18.36%). Its specific surface is 37.58 m<sup>2</sup> / g. The kinetics, thermodynamics and isotherms of adsorption have been used to understand the mechanism of adsorption. The results obtained show that the organic pollutant alone in solution (methylene blue (MB)) is adsorbed quite quickly. We obtained a decoloration yield greater than 90% after 40 min of adsorbate-adsorbent contact. The elimination of methylene blue is greater in a basic medium. The BM adsorption kinetics were modeled. The comparison of the correlation factors of the different kinetic models used has shown that the adsorption kinetics of the organic pollutant (MB) better match the pseudo second order kinetic model. Thermodynamics predicted a spontaneous endothermic surface reaction, due to the positive sign of  $\Delta H^0$  and the negative sign of  $\Delta G^0$ , obtained ( $\Delta H^0$  (kJ.mol<sup>-1</sup>) = 31.398;  $\Delta G^0$  (kJ.mol<sup>-1</sup>) = -12.635). Analysis of adsorption isotherms allowed us to show that the adsorption of methylene blue on clay is physisorption type and in monolayer. The experiments were also performed with an aqueous solution containing both methylene blue and cadmium ions. After a contact time of 120 min, 60% of the cadmium ions are adsorbed on the clay against only 20% of methylene blue. Thus, clay preferentially eliminates trace metal elements (Cd<sup>2+</sup>) compared to organic pollutants (methylene blue).

*Keywords: Green clay; methylene blue; cadmium ions; adsorption.*

## 1. INTRODUCTION

Increased industrial activities have raised many concerns about water pollution. In the textile and mining industries, the intensive use of dyes and heavy metals contaminates water resources. Most of these types of pollutants are hardly biodegradable [1-3]. They are qualified as major pollutants [4-6]. Therefore, the discharge of wastewater, without prior treatment, containing dyes and metallic trace elements can cause significant damage to human health and the environment. It is therefore essential to propose physicochemical techniques to eliminate them.

Common chemical processes used for wastewater treatment are electrochemical processes, photocatalytic processes and Fenton processes. [7-11]. Most of these methods are expensive and generate derivatives that are sometimes more toxic than the initial products themselves [12,13]. Thus, the physical process, based on the phenomenon of adsorption, presents itself as a much more interesting alternative. Indeed, adsorption is a technique characterized by its simplicity of design and operation, its relatively low cost and its efficiency [14,15]. Several research studies on the removal of pollutants (organic and inorganic) from wastewater use agricultural by-products, biological materials or residues from industrial transformation processes [16-18]. But the complexity of preparing adsorbents from this type of material sometimes limits their applications. Thus, the need to use adsorbents taken in their natural state and without any chemical or

physical modification, becomes a real issue. From this perspective, the use of clay as an adsorbent is of great interest.

Clay materials are good adsorbents which have a high cation exchange capacity and a large specific surface area given the small particle size. Clays have the advantage of being available and inexpensive. Their large specific surfaces therefore promote important reactions in water and soil. Such properties justify the use of clay as an adsorbent for the removal of a wide variety of pollutants from wastewater [19-20].

In this work, we are interested in the study of the simultaneous adsorption of methylene blue and cadmium ions on green clay in the region of Marahoué (Ivory Coast). To begin with, we first studied the behavior of clay in the presence of methylene blue alone in solution, then in the presence of a solution containing both methylene blue and cadmium ions. This adsorbent was used in its raw state, without any chemical or physical treatment. We were particularly interested in studying the equilibria relating to the kinetics and thermodynamics of adsorption to predict the mode of fixation.

## 2. MATERIALS AND METHODS

### 2.1 Raw Material

The clay used in this study was collected in the town of Bouaflé (6° 59 ' 00 " north, 5° 45 ' 00 " west) located in the Marahoué region in central Côte d'Ivoire. Before use, the clay collected was

crushed in a mortar and then sieved through a 100  $\mu\text{m}$  sieve.

## 2.2 Chemical Reagents

Methylene blue ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ , 99%) and sodium hydroxide (NaOH, 99%) from Fluka SA were used as reagents. We also used sulfuric acid ( $\text{H}_2\text{SO}_4$ , 96%) and cadmium chloride hemi (pentahydrate) ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ), supplied by Scharlau Chemie. All of these reagents were used without purification. Distilled water served as the solvent for the preparation of solutions in all of our experiments.

## 2.3 Characterization of Clay

The structural properties of the clay were determined using an X-ray diffractometer (Bruker D8 Discover Diffractometer, Cu K $\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ) set at 40 kV and 100 - 200 mA in the range  $10^\circ$  to  $70^\circ$  ( $2\theta$ ). The chemical composition of the clay was determined by X-ray fluorescence spectrometry (Epsilon 4, pulp / XRF). To determine its specific surface, the samples were degassed at  $150^\circ\text{C}$  for 16 hours using the Micromeritics TriStar II instrument.

## 2.4 Adsorption Experiments

Adsorption tests were performed in the dark. Different temperatures have been set ( $25$ ,  $50$ ,  $70$  and  $80^\circ\text{C}$ ). In 50 mL of synthetic waste water (methylene blue), we added various masses of clay (0.025; 0.05; 0.1; 0.15 and 0.2 g). Concentrations of synthetic water were between 0 and 50 mg / L (methylene blue concentration). For cadmium ions, a 0.01 M solution was prepared from the commercial product (Cadmium dichloride hemi pentahydrate  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ). In 1 liter of this solution, 10 mg of methylene blue was added, in order to obtain synthetic wastewater "methylene blue + cadmium ions". To follow the discoloration of the methylene blue over time, 2 mL of synthetic wastewater was regularly taken and then analyzed with a spectrophotometer (JENWAY 7315), at the maximum wavelength  $\lambda_{\text{max}} = 655 \text{ nm}$ . The determination of cadmium ions ( $\text{Cd}^{2+}$ ), was carried out using an atomic absorption spectrometer (Analytic Jena, ZEE nit 700), at the wavelength  $\lambda_{\text{Cd}} = 228,8 \text{ nm}$ .

The adsorption efficiency of the pollutant was evaluated using equation (1) [19]:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where:  $C_0$  is the initial concentration of the pollutant and  $C_t$ , that at time  $t$  ( $C_t$ : residual concentration)

The concentration of residual dye in the reaction mixture was calculated using the calibration curve, the equation of which is given by (2):

$$A_{655} = 0.1431C_t + 0.1272 \quad (2)$$

Where:  $A_{655}$  is the absorbance of the sample at the wavelength 655 nm.

The quantity of adsorbed pollutant ( $q_e$ ) was calculated using the following equation (3) [19]:

$$q_e = \frac{V}{m}(C_0 - C_t) \quad (3)$$

Where:  $V$  is the volume of the synthetic wastewater solution used and  $m$  the mass of adsorbent.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of Clay

#### 3.1.1 Chemical composition

The chemical compositions of the clay material are shown in Table 1.

The results of this table show that our clay is mainly composed of silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ). The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mass ratio is 3.7. According to the literature, this ratio is 1.18 for a pure kaolinite [21]. The difference between the value of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, obtained in the context of our clay and that of the literature, suggests several additional sources of silica. Thus, the excess silica could come from quartz and / or so-called type 2/1 compounds (illite, muscovite ...). In 2/1 clays, due to the numerous substitutions, the values of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mass ratio are generally between 2 and 4 [22]. The contents of iron oxide (8.74% de  $\text{Fe}_2\text{O}_3$ ), of potassium (3.89% de  $\text{K}_2\text{O}$ ) and of magnesium (2.44% de  $\text{MgO}$ ), are relatively high in our clay. According to the literature [21,23], the iron present in clay can substitute for  $\text{Si}^{4+}$  and / or  $\text{Al}^{3+}$  cations in tetrahedral and / or octahedral layers. It can also be in the form of oxy-hydroxides, namely goethite ( $\alpha\text{-FeOOH}$ ), and / or oxides such as hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\gamma\text{-Fe}_2\text{O}_3$ ). Potassium and magnesium may be part of the structure and inter-foliar space of type 2/1

compounds, respectively, suggesting the presence of illite ( $KAl_2Si_3AlO_{10}(OH)_2$ ) and dolomite ( $MgCa(CO_3)_2$ ). The relatively low levels of oxides such as CaO,  $TiO_2$ , MnO,  $Na_2O$ ,  $Cr_2O_3$  and  $P_2O_5$  could suggest the presence of impurities in the clay collected.

### 3.1.2 Mineralogical composition

The mineralogical composition of the clay sample was identified by X-ray diffraction (Fig. 1).

Fig. 1 shows the diffractogram obtained, it should be noted the presence of peaks characteristic of kaolinite ( $Al_2Si_2O_5(OH)_4$ ) at angles  $2\theta$ : 12.46° and 25.23°; de l'illite ( $KAl_2(Si_3Al)O_{10}(OH)_2$ ) at angles  $2\theta$ : 8.8°, 27.92°, 29.94°, 31.32°, 32.08° and 42.52°; quartz ( $SiO_2$ ) at  $2\theta$ : 20.9°, 26.7°, 39.54° and 40.36°. In addition to these peaks, the diffractogram also reveals the presence of iron oxy-hydroxides (hematite ( $\alpha-Fe_2O_3$ ) and goethite ( $\alpha-FeOOH$ )) characterized by peaks observed at  $2\theta$ : 23.98° and 35.08° for hematite and at  $2\theta$ : 21.78°, 36.02° and 36.64° for goethite. The results obtained in XRD are consistent with those of chemical analysis. Calculations carried out, taking into account the results of the chemical analysis and the ideal chemical

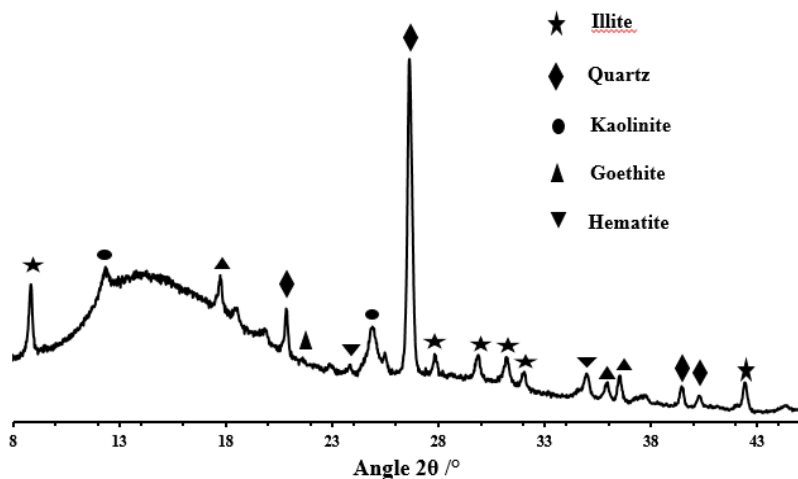
composition of the phases detected by X-ray diffraction, made it possible to estimate the mineralogical compositions of the clay used [24]. Thus, our clay is composed of 40.23% quartz, 32.94% illite, 8.47% kaolinite and 18.36% iron oxy-hydroxides.

### 3.1.3 Specific surface

The clay used in this study has a specific surface area of 37.58  $m^2 / g$ . This value is higher than that generally observed (10 to 30.2  $m^2 / g$ ) for kaolinitic type clays [25,26]. The relatively high value of the specific surface would be due to the relatively high content of iron compounds present in this clay. The presence of iron compounds in the texture of the clay leads to a slight increase in its specific surface by 4 to 8% [27]. This phenomenon was observed by Soro and Sei during their work on natural clays from Côte d'Ivoire [23,28]. The author Soro observed a linear change in the specific surface area of kaolinitic clays as a function of the iron content. He showed during this work that for an iron oxide content of about 9%, the initial specific surface of kaolinitic clays is multiplied by a factor of 3.8 compared to the specific surface of the material which does not contain no iron.

**Table 1. Chemical and mineralogical composition of Bouaflé clay**

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	TiO <sub>2</sub>	CaO	MnO	Na <sub>2</sub> O	Cr <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
%	59.07	16.01	8.74	3.89	2.44	0.46	0.30	0.07	0.07	0.05	0.03
oxide											
%	Illite (32.94%) ; kaolinite (8.47%) Quartz (40.23%) ; Iron oxy hydroxides (18.36%)										
phase											



**Fig. 1. XRD graph of the clay**

### 3.2 Behavior of Clay in the Presence of Methylene Blue Alone in Solution

#### 3.2.1 Influence of contact time

Fig. 2 shows the change in the amount of methylene blue adsorbed as a function of contact time.

This figure shows that the equilibrium retention capacities increase with increasing initial concentration and contact time. For the different concentrations used, the amount of pollutant (methylene blue) adsorbed on the clay hardly varies after 40 min. Thus, after 40 min, the majority of the clay adsorption sites are saturated with methylene blue. This result suggests the existence of repulsive forces between the adsorbed methylene blue and that in solution, thus preventing the superposition of the MB layers on the clay.

#### 3.2.2 Influence of the clay mass

To study the influence of clay mass on the rate of methylene blue removal, different experiments were performed using the following amounts of adsorbent: 0.025; 0.05; 0.1; 0.15 and 0.2 g. Fig. 3 shows the results obtained.

For all the quantities of clay used, the elimination rate is high ( $\eta > 90\%$ ). Among the clay masses used, the masses of 0.1 and 0.15 g make it

possible to obtain an almost total elimination of the pollutant, after 40 min ( $\eta \approx 100\%$ ). Thus, in the case of our study, the optimal mass of clay necessary for the effective removal of methylene blue (10 mg / L) would be between 0.1 and 0.15 g. For quantities of clay greater than 0.15 g, a decrease in the rate of elimination of methylene blue is observed. This may be due to the difficulty of the MB molecules in reaching the adsorbent sites of the clay due to the clutter caused by the excess clay mass [29]. The greater the quantity of clay, the greater the agglomeration phenomenon of the clay particles.

#### 3.2.3 Influence of pH

In this work, we followed the evolution of the rate of elimination of methylene blue (10 mg / L) in the presence of 0.1 g of clay, at pH equal to 3; 5; 6.9; 10 and 12 (Fig. 4).

In general, when the pH of the solution is increased, the rate of MB elimination increases. The adsorption of MB on clay is very important when the pH is greater than or equal to 10 ( $\text{pH} \geq 10$ ). The elimination of methylene blue would therefore be favorable in a basic medium. In an acidic environment, there would be competition between the dye and the  $\text{H}^+$  ions for the occupation of the clay adsorption sites [19]. This competitive effect becomes negligible when the concentration of  $\text{H}^+$  ions decreases, that is to say in a basic medium.

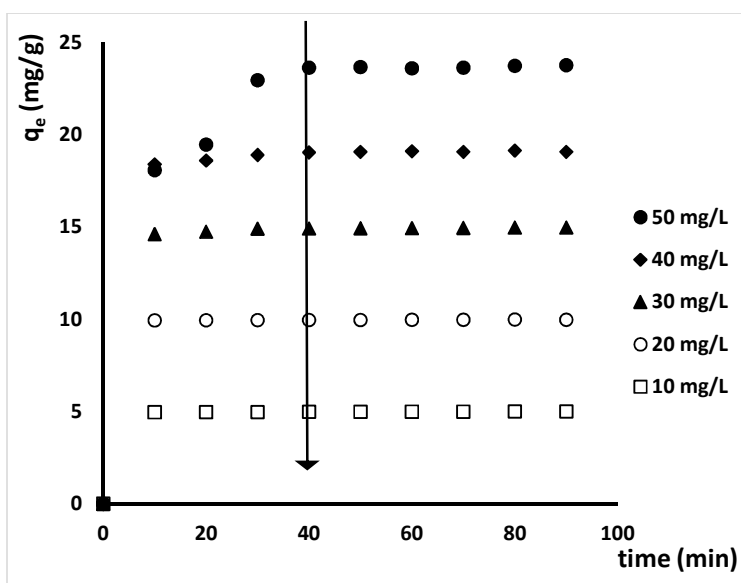


Fig. 2. Influence of the contact time; pH = 6.9 and T = 25°C

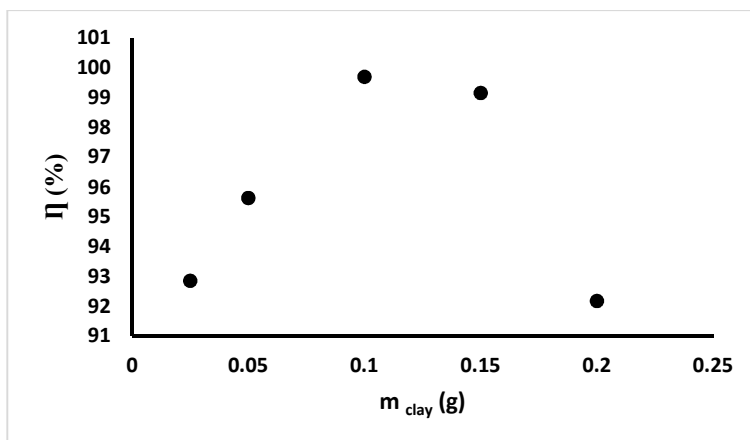


Fig. 3. Influence of the clay mass; pH = 6.9; t = 40 min and T = 25°C

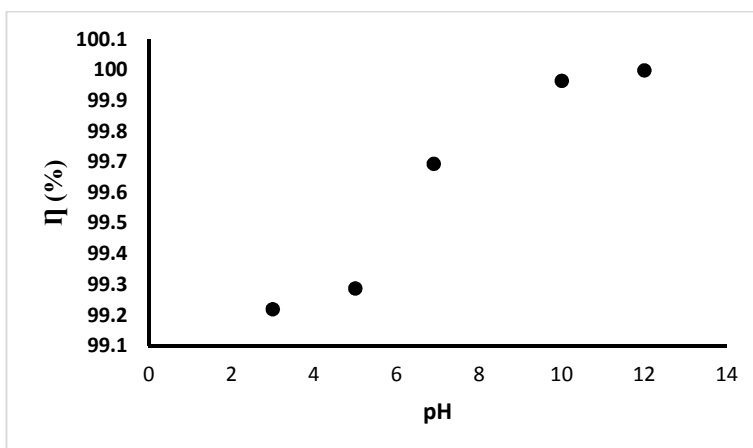


Fig. 4. Influence of pH; t = 40 min and T = 25°C

### 3.2.4 Influence of temperature

In order to understand the thermodynamic phenomenon of the adsorption of the dye by the clay, we carried out discoloration experiments by varying the temperature of the solutions. Fig. 5 illustrates the evolution of the BM elimination rate as a function of temperature.

As the temperature increases, the rate of elimination also gradually increases. Thus, the adsorption of methylene blue on clay would be an endothermic process. The increase in temperature increases the rate of diffusion of methylene blue molecules through the outer boundary layer and into the clay particles, due to the decrease in the viscosity of the solution [30].

### 3.2.5 Adsorption isotherms

For the modeling of adsorption isotherms, the following three models were used: Langmuir,

Freundlich and Temkin. The linear form of the Langmuir isotherm is given by equation (4):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}} \quad (4)$$

Where  $C_e$  (mg/L) is the equilibrium concentration,  $q_e$  (mg/g) is the amount adsorbed at equilibrium,  $q_{\max}$  (mg/g) is the maximum amount adsorbed and  $K_L$  is the Langmuir constant. The application of this linear form to our experimental results, allowed us to obtain Fig. 6.

The correlation coefficient ( $R^2$ ) and the Langmuir parameters determined from Fig. 6, are grouped together in Table 2.

The modeling of the Freundlich isotherm was made possible through the use of the linear form, equation (5):

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (5)$$

Where:

$K_F$  and  $1/n$  re the Freundlich constants. They characterize the efficiency of a given adsorbent with respect to a given solute. Fig. 7 shows that the representation of  $\ln q_e$  versus  $\ln C_e$  leads to a line of equation (6):  $y = 0.2872x + 2.895$ , slope  $1/n$  and ordinate at the origin  $\ln K_F$ . The Freundlich parameters as well as the correlation coefficient are given in Table 2.

Modeling of experimental results by Temkin's model:  $q_e = \left(\frac{RT}{B}\right) \ln K_T + \left(\frac{RT}{B}\right) \ln C_e$  (7) yielded Fig. 8. The numerical values of  $K_T$  and  $B$  (Temkin's parameters) calculated, respectively, from the intercept and the slope of the line of the isotherm, are shown in Table 2.

From Tables 2, it appears that the correlation coefficient  $R^2$  is equal to 0.994; 0.850 and 0.931, respectively for the Langmuir, Freundlich and Temkin isotherms. Thus, the Langmuir model would be the model that best describes our experimental results. Therefore, the adsorption sites on the clay surface are all strongly equivalent; each of these sites can only bind a single methylene blue molecule; adsorption occurs in a single layer and there is no interaction between the adsorbed molecules [31].

The value of  $(n)$  obtained from the Freundlich model is greater than 1 ( $n = 3.482$ ) indicates that the adsorption is favorable and physical [32,33].

### 3.2.6 Kinetic study

The kinetic study of the retention of methylene blue by clay was carried out according to the following three models:

- The pseudo first order model [34] (8):

$$\ln \left[ \frac{q_e - q_t}{q_e} \right] = -k_1 t$$

- The pseudo second order model [35] (9):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

- The model of intraparticle diffusion [35] (10):  $q_t = k_{int} t^{1/2}$

With  $k_1$ ,  $k_2$  and  $k_{int}$ , respectively the kinetic constants of pseudo first order, pseudo second order and intraparticle diffusion. Fig. 9, 10 and 11 summarize the results obtained. According to the literature [36], the value of the correlation coefficient ( $R^2$ ) makes it possible to choose the model that best describes the study of adsorption kinetics. The higher the value of  $R^2$ , the better the model for studying the adsorption process.

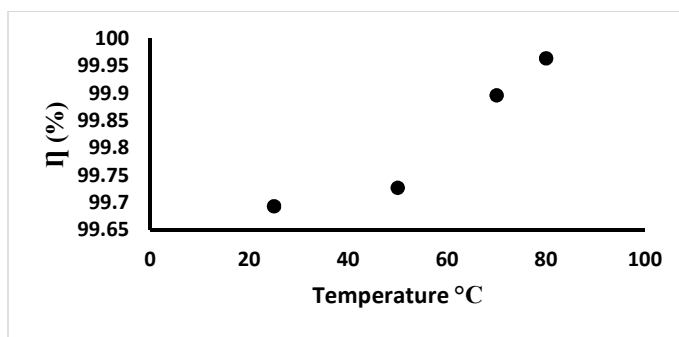


Fig. 5. Influence of temperature; pH = 6.9; t = 40 min and T = 25 ° C

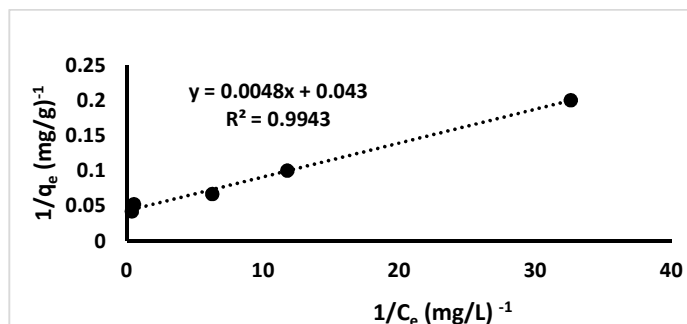


Fig. 6. Langmuir isotherm for BM adsorption onto clay

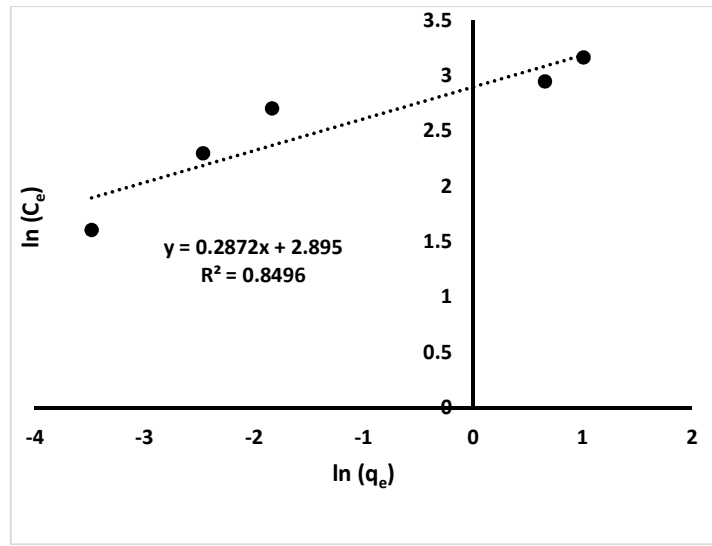


Fig. 7. Freundlich isotherm for BM adsorption onto clay

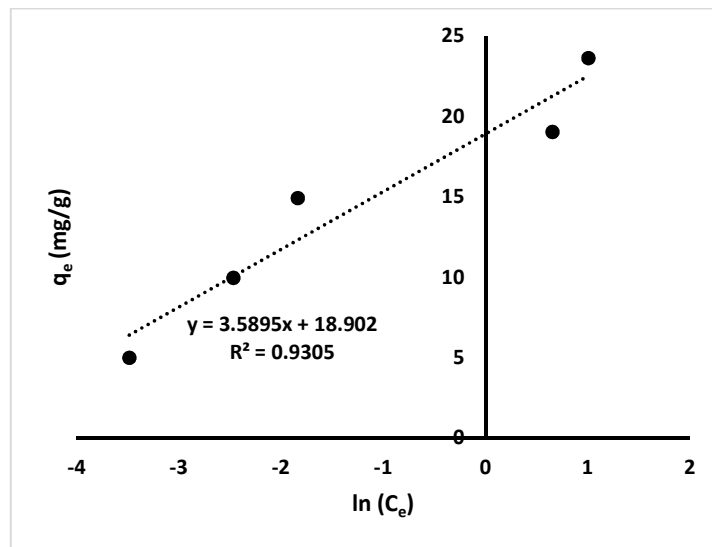


Fig. 8. Temkin isotherm for BM adsorption onto clay

Table 2. Equilibrium adsorption isotherm parameters for methylene blue

Model	Parameters	Value
Langmuir	$q_{max}$ (mg/g)	23.256
	$K_L$ (L/mg)	8.958
	$R^2$	0.994
Freundlich	$1/n$	0.287
	$n$	3.482
	$K_F$ (mg/g)	18.084
Temkin	$R^2$	0.850
	$K_T$ (L/mg)	193.623
	$B$ (J/mol)	3.590
	$R^2$	0.931



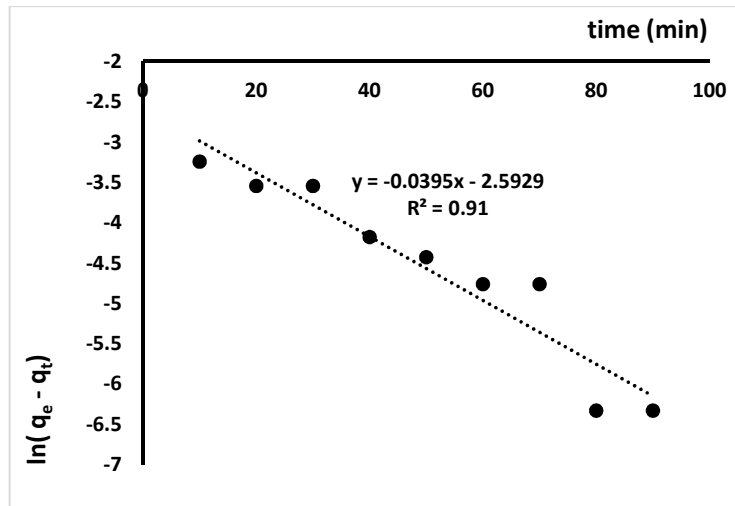


Fig. 9. Pseudo first order kinetic model

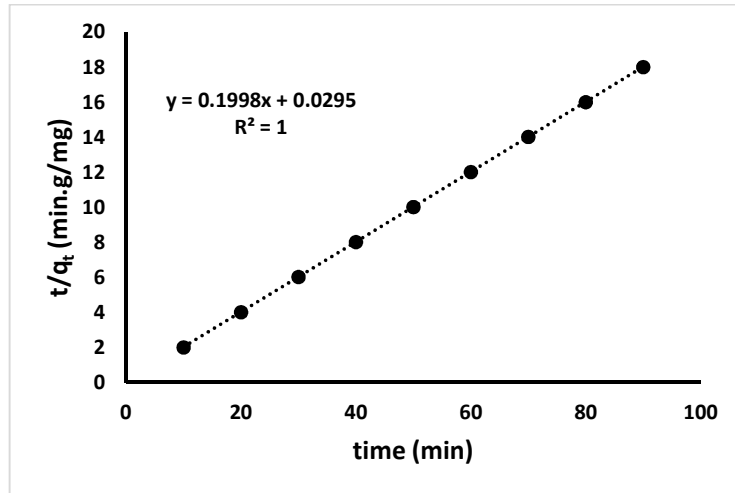


Fig. 10. Pseudo second order kinetic model

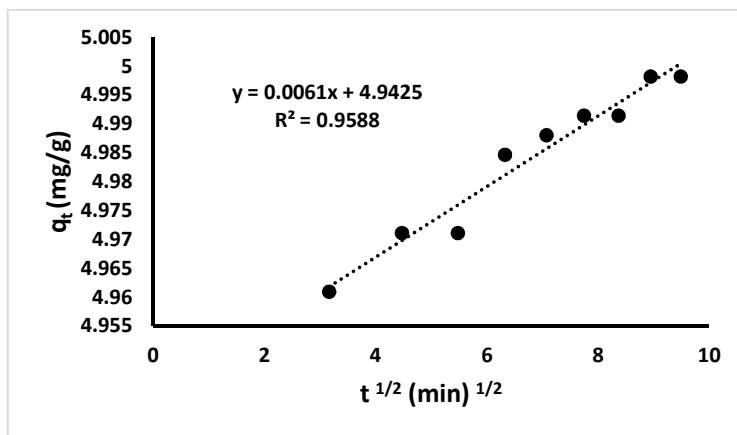


Fig. 11. Model of intra-particle diffusion

The kinetic parameters determined from the lines of the different models used are collated in Table 3.

From the results shown in Table 3, we notice that the model which has the highest correlation factor is that of the pseudo-second-order model ( $R^2 = 1$ ). Thus, the pseudo second order model is the one that best describes the process of adsorption of methylene blue on clay. Also, the value of  $q_e$  calculated from this model is very close to that determined experimentally. This confirms the choice of this model for the kinetic study of MB adsorption on clay.

### 3.2.7 Thermodynamic parameters

The thermodynamic parameters of the adsorption reaction of methylene blue on Bouafilé clay, namely standard free enthalpy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) were determined from equations (11), (12) and (13) [37]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad (11)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

$$K_d = \frac{q_e}{C_e} \quad (13)$$

Where  $K_d$  represents the distribution coefficient. The curve  $\ln K_d$  versus  $1/T$  has been shown in Fig. 12.

The results of the thermodynamic parameters are reported in Table 4.

The analysis of these thermodynamic parameters has shown that the adsorbate adsorption process (methylene blue) on the adsorbent (clay) takes place as a spontaneous reaction, regardless of the temperature ( $\Delta G^\circ < 0$ ) [31]. The variation of the free enthalpy ( $\Delta G^\circ$ ) changes inversely with the temperature of the solution. Thus, increasing the temperature further promotes the absorption process of methylene blue on the clay. The positive sign of the standard enthalpy  $\Delta H^\circ$ , confirms that the adsorption process is endothermic. The calculated value of  $\Delta H^\circ$  is less than 40  $\text{kJ}\cdot\text{mol}^{-1}$ . This result, which shows that it is a physisorption [38,39]. The positive sign of entropy ( $\Delta S^\circ$ ) indicates a disorder of methylene blue molecules at the solid-solution interface during the adsorption process [40,41].

### 3.3 Behavior of Clay in the Presence of Methylene Blue and Cadmium Ions in Solution

#### 3.3.1 Simultaneous adsorption study

For the study of the simultaneous adsorption of methylene blue and cadmium ions, we followed the evolution of the rate of elimination of these pollutants as a function of time (Fig. 13).

**Table 3. Kinetic parameters of MB adsorption on clay**

<b>Pseudo first order</b>	$k_1(\text{min}^{-1})$	0.0395
	$q_{e,\text{cal}}(\text{mg}\cdot\text{g}^{-1})$	0.0748
	$q_{e,\text{exp}}(\text{mg}\cdot\text{g}^{-1})$	4.985
	$R^2$	0.91
<b>Pseudo second order</b>	$k_2(\text{g}\cdot\text{m}^{-1}\cdot\text{min}^{-1})$	1.356
	$q_{e,\text{cal}}(\text{mg}\cdot\text{g}^{-1})$	5.005
	$q_{e,\text{exp}}(\text{mg}\cdot\text{g}^{-1})$	4.985
	$R^2$	1
<b>Intra-particle diffusion</b>	$k_{\text{id}}(\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2})$	0.0061
	C	4.9425
	$R^2$	0.9588

**Table 4. Thermodynamic parameters**

$\Delta H^\circ (\text{kJ}\cdot\text{mol}^{-1})$	31.398			
$\Delta G^\circ (\text{kJ}\cdot\text{mol}^{-1})$	145.038			
$\Delta S^\circ (\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	298.15 K	323.15 K	343.15 K	353.15 K
	-12.635	-13.993	-17.631	-21.27

The analysis in Fig. 13 shows co-adsorption of methylene blue and cadmium ions. The adsorption of the dye is low compared to that of trace metal ions. After a contact time of 120 min, 60% of the cadmium ions are adsorbed on the clay against only 20% of methylene blue. This result shows the existence of a competition between the cationic dye (methylene blue) and cadmium ions ( $\text{Cd}^{2+}$ ) for the occupation of the clay adsorption sites. Cadmium ions would be the first to deposit on the clay compared to methylene blue. This leads to a decrease in the adsorption efficiency of methylene blue.

### 3.3.2 Kinetic study

In order to deepen the previous observations, we studied the adsorption kinetics of each

pollutant in the "methylene blue-cadmium ion" mixture, using the Blanchard model (pseudo second order). Figs 14 and 15 show the results obtained for BM and  $\text{Cd}^{2+}$ , respectively. The kinetic parameters calculated from the equations of the lines of Fig. 14 and 15 are reported in Table 5.

The data in this Table (5) show that in the case of a system containing several pollutants (MB +  $\text{Cd}^{2+}$ ), the mobility of cadmium ions is greater than that of methylene blue ( $k_2(\text{Cd}^{2+}) > k_2(\text{BM})$ ). This finding confirms that cadmium ions are deposited first on clay compared to methylene blue.

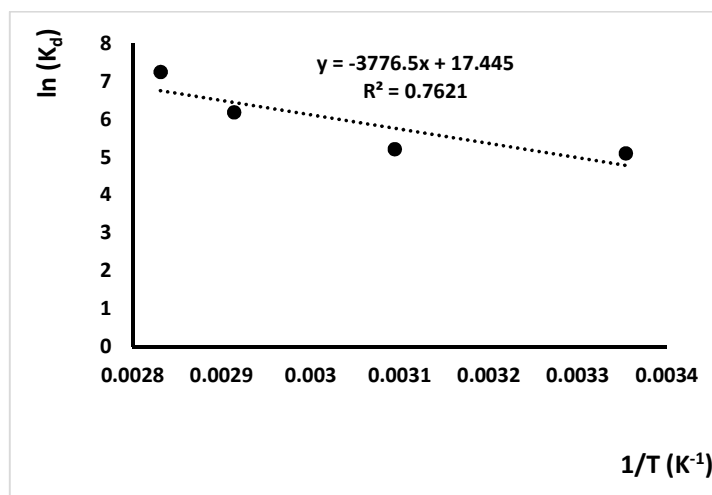


Fig. 12. Curve of  $\ln(K_d)$  versus  $(1/T)$  for the adsorption of MB on clay

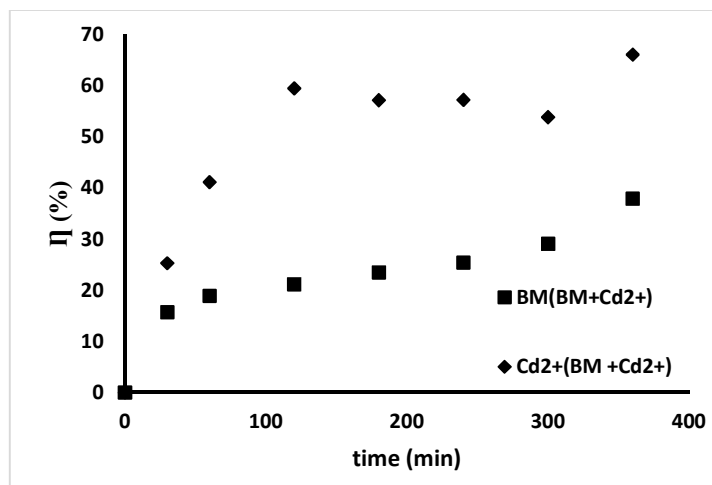


Fig. 13. Adsorption of methylene blue and cadmium ions on clay

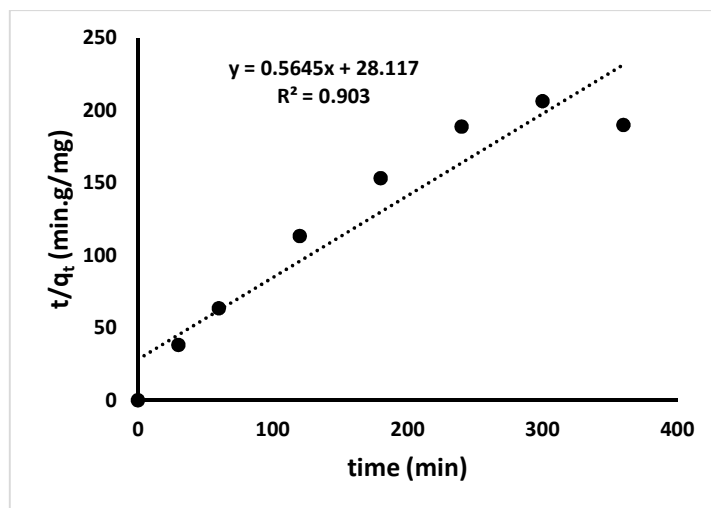


Fig. 14. Pseudo second order kinetic model of methylene blue in the mixture "MB-Cd<sup>2+</sup>"

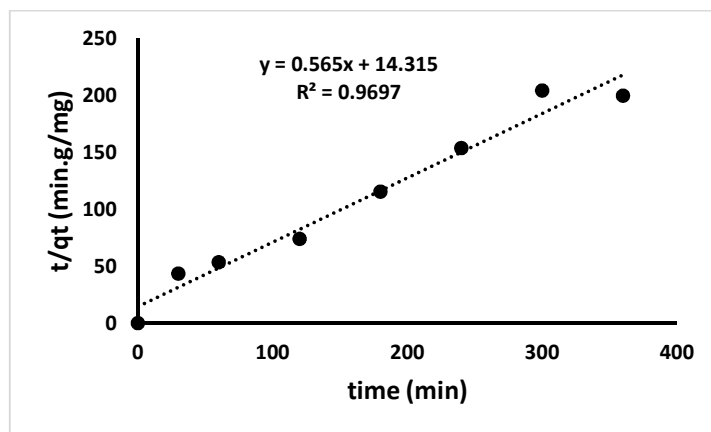


Fig. 15. Pseudo second order kinetic model of Cd<sup>2+</sup> in the "MB-Cd<sup>2+</sup>" mixture

Table 5. Kinetic parameters of adsorption of each pollutant on clay

	$k_2(g \cdot mg^{-1} \cdot min^{-1})$	$q_{e.cal}(mg \cdot g^{-1})$	$R^2$
BM (BM+Cd <sup>2+</sup> )	0.0113	1.771	0.903
Cd <sup>2+</sup> (BM+Cd <sup>2+</sup> )	0.0224	1.767	0.9697

#### 4. CONCLUSION

The present study has shown the possibility of upgrading clays from Côte d'Ivoire (Bouaflé) in the elimination of organic matter (methylene blue) and trace metal elements (cadmium ions) by adsorption.

The physicochemical characterization made it possible to show that the clay used is a clay

composed essentially of type 2/1 minerals such as illite (32.94%), type 1/1 kaolinite (8.47%), quartz (40.23%) and iron oxy-hydroxides (18.36%). The specific surface area measured (37.58 m<sup>2</sup> / g) is greater than those of kaolinitic type clays.

The effect of a few experimental parameters has been studied. The results obtained showed that the elimination of BM (alone in solution) is very

rapid and the contact time allowing maximum adsorption is 40 min. The optimum amount of clay to effectively adsorb methylene blue (10 mg / L) is between 0.1 and 0.15 g.

The quantity of pollutant adsorbed decreases with the pH of the solution because of the competition exerted by the H<sup>+</sup> ions. It increases the temperature of the experiment. The adsorption of methylene blue on clay is therefore favorable in a basic medium and is an endothermic process.

The isotherm which best describes the absorption process of methylene blue on clay is that of Langmuir and the ideal kinetic model to study this process is the pseudo second order model.

In the presence of several pollutants (methylene blue and cadmium ions), there is simultaneous adsorption of these on the surface of the adsorbent, with faster adsorption of trace metal elements (cadmium ions) than organic pollutants (methylene blue).

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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