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Discoloration of contaminated water by an industrial dye: Methylene Blue, by two Algerian bentonites, thermally activated

I.Feddal[1,2], Z.Taleb[1], A.Ramdani[1,3], H. Herbache[1], S.Taleb[1*]

[1] Laboratory of Materials & Catalysis, Faculty of Exact Sciences, Djillali Liabès university, BP 89, W-22000, SidiBel-Abbès, Algeria.
[2] Faculty of Sciences and Technology, Abdel Hamid IbnBadis, university, BP 188, W-27000, Mostaganem, Algeria.
[3]Department of Chemistry - Faculty of Sciences - University Dr. MoulayTahar - Saida 20000 Algeria.
* Corresponding author:safiataleb@yahoo.fr/safia.taleb@univ-sba.dz ; Tel.: +213560809933; Fax: +213 48742174.

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ABSTRACT/RESUME

Abstract: *In this work, we proceeded to a cationic dye removal of the textile industry wastewater discharge: methylene blue (MB) by adsorption on two types of local clays, type Montmorillonite sodium (AS) and calcium (AC) activated thermally at 300°C. Several parameters influencing MB adsorption process such as: (i) adsorbent-adsorbate contact time, (ii) clay mass, (iii) pH of the medium, (iv), initial dye concentration (v) and the temperature. The results obtained show that the maximum adsorption is achieved with a percentage of f discoloration of 99.49% and 98.51% and with an adsorption capacity of 450 mg/g and 240 mg/g for AC-300 °C and AS-300 °C, respectively. The acidity and basicity of the medium considerably affect the adsorption of this dye. The results deduced from the isotherm adsorption data show that the retention of methylene blue dye follows perfectly the Langmuir model. The thermodynamic parameters indicate that adsorption is endothermic, spontaneous and physical type.*

I. Introduction

Today, effluents of industrial, agricultural and domestic origin are increasingly loaded with pollutants that can be non-biodegradable. The impact of these pollutants is very harmful and constitutes a major environmental and health problem [1,2]. An awareness of the socio-economic actors, accompanied by a strict regulation, contributes in the fight against these organic pollutants [3]. Among the industries, we find that of textile with that of the tannery at the top of the list. These activities generate significant pollution in wastewater. These effluents are heavily loaded with acidic or basic dyes [4]. To this end, the protection of human health and the environment has become a major concern for our society, forcing researchers to develop new techniques for the treatment and purification of wastewater [5]. Current research is then directed to several treatment processes [6-10]: coagulation and flocculation, biodegradation, membrane filtration, chemical oxidation, ozonation, ion exchange, electrochemical methods, and adsorption. It can also be a good alternative for the removal of dyes and other organic pollutants [11,12]. To do this, various inexpensive adsorbent materials can be used (clays, zeolites, activated alumina, apatites, sludge, biomasses, agricultural residues, industrial by-products and activated carbon, etc.) [13,14]. For this purpose, we propose the removal of the basic dye (methylene blue) by adsorption on calcium and sodium clays, which are activated thermally at 300 °C, before their use. They are known by their abundance in

nature, their multiple physicochemical properties. A series of experiments was carried out to study the influence of certain parameters such as: (i) contact time adsorbent-adsorbate (ii) mass of clay, (iii) pH of the solution, (iv) initial concentration of dye (v) and finally temperature.

II. Materials and methods

II.1. Adsorbents

Two adsorbents used are Montmorillonite type, supplied from Roussel (Maghnia, Algeria). The preparation of thermal activated bentonite was carried out by calcination of sodium and calcium bentonite at 300°C in ash oven of brand Nabertherm GmbH -LV9/11 B180 (from 30 °C to 3000 °C).The two types of heat-activated calcium and sodium clays are noted: AC-300 °C and AS-300 °C, respectively.

II.2. Choice of adsorbate

Methylene blue BM or bis (dimethylamino) -3,7 phenazathionium chloride, also known as methylthioninium chloride, is an organic compound of the chemical formula C16H18ClN3S, which belongs to the family of Xanthines [15]. It has a molar mass of 319.86 g/mol and a solubility of 50 g/L in water at 20 ° C and 10 g/L in ethanol at 20 ° C. Its structural formula is shown in the following figure (Figure 1).

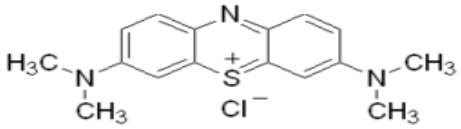

Figure 1.*Molecular Structure of Methylene Blue*.

II.3. Experimental protocol:

The experimental study methylene blue adsorption was carried out in synthetic dilute solutions of methylene blue in batch, by dissolving a specific adsorbent mass in a known concentration solution of methylene blue, during a set time. After such time, the liquid phase is recovered and filtered, and the dye residual concentration were determined from the absorbance analysis (A) which were followed using UV-Visible spectrophotometer, Perkin-Elmer's (model Lamda 45), at 664 = ג nm. The adsorption equilibrium was achieved by varying; initial dye concentration, 100-1000 mg /L; contact time, from 0 to 120 min; mass of the adsorbent, from 25 to 200 mg; pH, 4-10 and temperature, 25 to 80 ° C.

The percentage of the discoloration R (%) and qe amount of dye adsorbed (mg/g) of the MB were calculated using the following equations, respectively:

$$\%\,\text{adsorption} = \frac{(C_i - C_{eq})100}{C_i} \qquad \textbf{(1)}$$

$$q_e = \frac{X}{m} = \frac{(C_i - C_{eq})V}{m} \qquad \textbf{(2)}$$

Where C i is the initial concentration (mol/L), Ceq is the equilibrium concentration (mol/L), V is the volume of the solution (L), m is the mass of adsorbent used (g), and X number of grams of methylene blue adsorbed (mg).

II.4. Characterization of adsorbents

II.4.1. pH measurement

The measurement of the pH of suspension clay is very important for the determination of the surface nature of our samples. For this purpose, 1 g of adsorbent is dissolved in 100 mL of distilled water. The solution is stirred for 24 hours and then filtered. The pH of the filtrate is measured using a pH meter (CRISON micro pH 2001) with a previously calibrated glass electrode. The results obtained show that the pH values for both of clays after calcination AC-300 °C and AS-300 °C are 7.83 and 6.55, respectively.

II.4.2. Point of Zero Charge (pHpzc)

The surface charge of materials, resulting from acid-base equilibria, depends on the pH and ionic strength of the solution with which the material is in suspension. This charge can be negative, positive or zero [14]. An important characterization of the surface is the zero charge pH (pH_{ZPC}): which defines the pH for which the charge of the surface is zero.

For the determination of the pH_{ZPC} of materials (AC-300°C and AS-300°C), the experimental tests were carried out by adding in volumetric flasks a volume of NaCl solution 0.1M (initial pH was adjusted from 2 to 12 by adding NaOH) with a precise amount of sodium and calcium clays of 0.2 g. After stirring magnetically for 6h, the final pH was measured and plotted against the initial pH. The pH corresponding to the point of intersection with the pH (final) =pH (initial) was taken as the pH_{PZC} of the material.

The pH_{pzc} values of AC-300 °C and AS-300 °C are 11.6 and 5.11, respectively. When the pH is less than the value of pH_{pzc}, the surfaces are charged positively when the pH is higher than the value of pH_{pzc}, the surfaces are negatively charged.

II.4.2. Infrared Spectroscopy:

The infrared spectra are made using a PerkinElmer Frontier FTIR spectrophotometer over the range 4000-400 cm^{-1}.

Characterization of sodium clay (AS) and calcium Clay (AC), AC-300°C and AS-300°C before and after adsorption of MB was carried out by IR spectroscopy. The IR spectra obtained are grouped together in figures 2 and 3.The results obtained from the both clays AS and AC show the main characteristic bands at 3,580 cm^{-1} and 3,620 cm^{-1} attributed to the Fe and Al bond for OH of clays 2:1, respectively. Moreover, the band to 915 cm^{-1}, indicates the deformation vibrations of the OH-Al bonds clay [16].

Another band located at 1630 cm^{-1} corresponds to the deformation vibrations of the H_2O molecules adsorbed between the sheets [16].

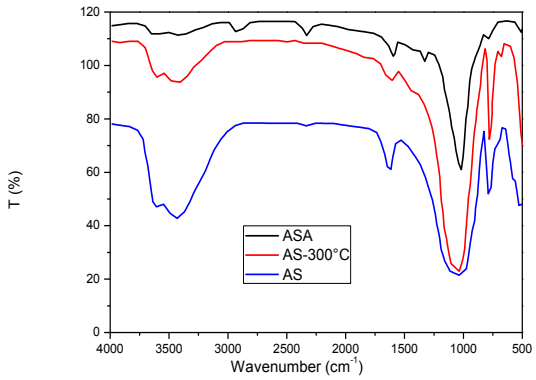

Figure 2. *FTIR spectra of AS, AS-300°C and ASA.*

Weak bands at 875 and 1460 cm^{-1} characteristic of the vibrational frequencies of carbonate ions CO_3^{2-} in calcium clay.

After calcination of the sodium and calcium clays at 300°C (AC-300°C and AS-300°C), it can be observed a significant decrease in the bands intensity characteristic of the OH group of the surface water at 3620 cm^{-1} and a slight decrease in the valence bands of adsorbed water (between sheets) 1630 cm^{-1} as evidence of water disappearance at this calcination temperature at 300°C.

Comparison of the IR spectra of the calcined clays before and after adsorption of MB shows a significant decrease in the characteristic bands of the clays and new bands appear. The band at 1340 cm^{-1} is attributed to CH_3-N-CH_3 aliphatic amines [17]. The valence band of the C=N bond(1592 cm^{-1}) is more intense in ACA and ASA clays. These results confirm the fixation of MB on both types of clays [17].

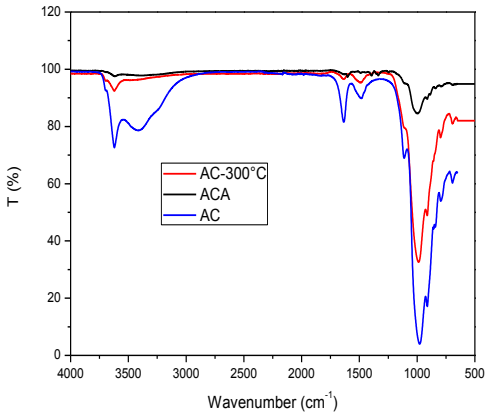

Figure 3. *FTIR spectra of AC, AC-300°C and ACA.*

III. Results and discussion

III.1. Batch adsorption studies

III.1.1.Effect of contact time

The influence of the stirring time of methylene blue adsorption by clay is a very important step in determining the time required to reach the maximum adsorption equilibrium [18]. Figure 4 shows the evolution of the yield of the discoloration on the two types of clays AC-300°C and AS-300°C as a function of the contact time.

The results obtained show that the adsorption is quite fast. The removal efficiency of the MB increases with the contact time and then it stabilizes; the maximum discoloration is obtained within 20 minutes and 30 min for AC-300°C and AS-300°C. Indeed, the maximum adsorption is achieved with a percentage of discoloration of 99.49% and 98.51% for AC-300°C and AS-300°C, respectively.

The difference in the degree of adsorption may be due to the fact that, at the beginning of the adsorption, all the sites of the adsorbent surface are free and accessible, so the MB molecules are easily adsorbed with these sites [19]. As a result, the removal of BM stabilization after the fixed contact time between the clay and this dye (saturation), depends on the number of vacant sites on the surface of the clay. Similar results have been reported for adsorption of Methylene Blue on clays [13,20].

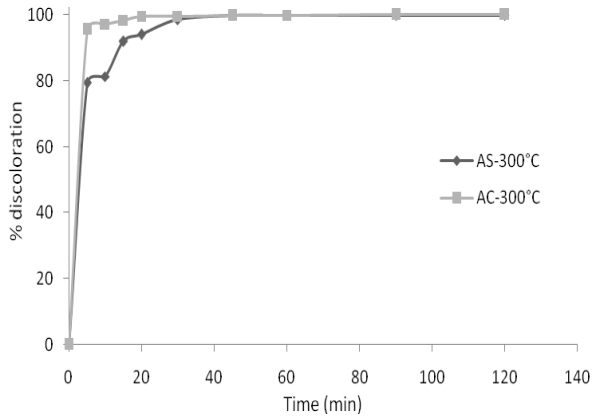

Figure 4.*Effect of contact time on adsorption of methylene blue by AC-300°C and AS-300°C.*

III.1.1.Effect of pH

Analysis of the results of figure 5 shows that adsorption increases with pH up to pH = 6.6 and then decreases considerably at basic pH. In addition, the rate of dye removal is very high with calcium clay than with sodium clay. This can be explained by the charge properties of the functional groups present on the surface of clay minerals [21].

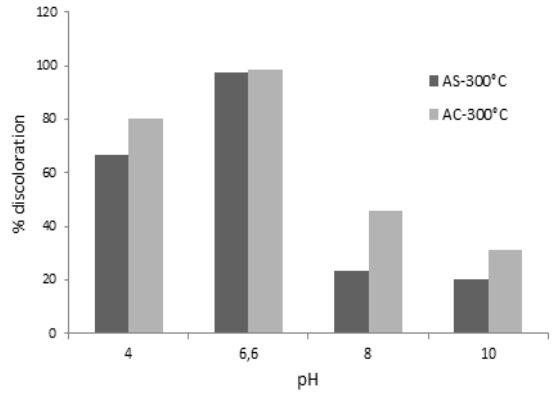

Figure 5.*Effect of pH on adsorption of methylene blue by AC-300°C and AS-300°C.*

At low pH and below pH_{pzc}, the number of adsorption sites positively charged on the surface of the clay increases thanks to the addition of the H^+ cations, and the number of negatively charged site decreases, which disadvantages the adsorption of the cationic dye MB. As the pH increases above pH_{pzc}, new reaction sites can deprotonate and contribute to increasing the reactivity of the medium. Thus, methylene blue molecules in solution will in turn be attracted to the surface. This is in agreement with the results obtained with kaolinite from India [22] and with zeolite adsorbents [13].

III.1.3.Effect of the adsorbent mass

From figure 6, it can be observed that the percentage of dye removal increases proportionally as the mass of adsorbents until reaching an equilibrium starting from 0.1g. Beyond this value, we do not find any eloquent change since the discoloration efficiency remains unchanged. The maximum removal of methylene blue is over 99% for both types of adsorbent. The optimal mass deduced is 0.1g.

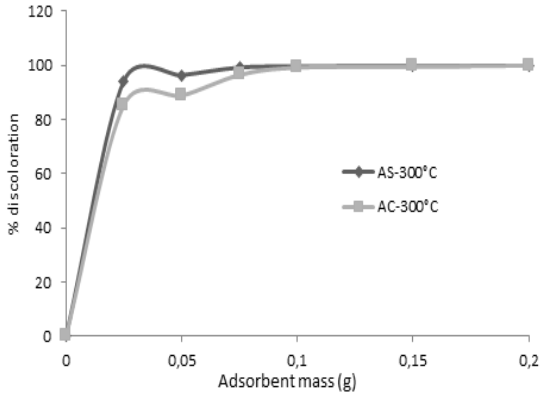

Figure 6. *Effect of adsorbent mass on MB adsorption.*

III.1.4. Effect of temperature

In order to study the effect of temperature on the MB adsorption process on both types of clays, a series of experiments were carried out at different temperatures between 25 and 80°C.

The other experimental parameters are previously optimized. The rate of MB removal enhanced from 80% to 95% when the temperature increases from 25°C to 80°C, which shows that the adsorption of methylene blue on both types of clays is an endothermic process.

III.2.Adsorption isotherm

The adsorption isotherms are evaluated by the graphical plot of relation qe = f (Ce). The curves obtained are illustrated in figures 7 and 8.

From these two figures, we find that the adsorption capacity increases with the equilibrium concentration of adsorbate. The isotherm reveals a rapid adsorption then resumes its pace attaining plateau until saturation of the adsorption sites. The equilibrium between the different phases is achieved by forming a monolayer of MB dye on the surface. Calcium clay (AC-300°C) has a high adsorption capacity of about 450 mg/g. While the adsorption capacityis 240 mg/g in sodium clay (AS-300°C).

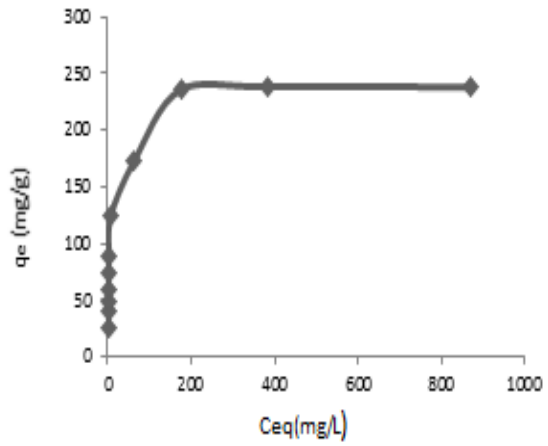

Figure 7. *Adsorption isotherm of methylene blue onto AS-300°C*

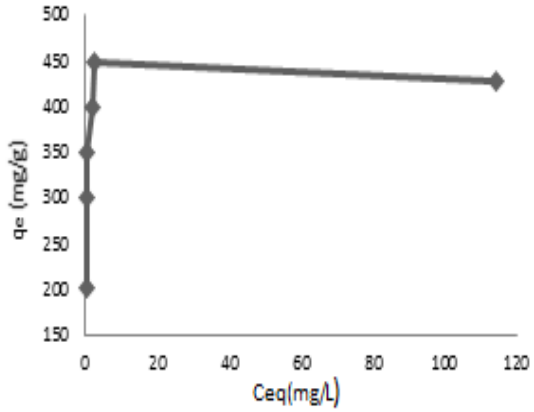

Figure 8. *Adsorption isotherm of methylene blue onto AS-300°C*

The linearization of the adsorption isotherms was carried out by applying the Langmuir, Freundlich and Temkin models. The results and plots are made using the following equations [13,23,24]:

$$\frac{Ce}{qe} = \frac{Ce}{q_{\max}} + \frac{1}{K_L q_{\max}} \qquad \textbf{(3)}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln Ce \qquad \textbf{(4)}$$

$$q_e = B\ln A + B\ln C_e \qquad \textbf{(5)}$$

Where: Ce: The equilibrium concentration (mg/L), qe: The amount adsorbed per gram of adsorbent (mg/g), K_L: Langmuir constant (L/mg), K_F: Freundlich constant (L/mg), Qmax: Maximum adsorbed amount per gram of adsorbent (mg/g), n: Freundlich constant characteristic of the effectiveness of adsorbents towards given solutes, B: Temkin constant for heat of adsorption, A: Adsorption equilibrium constant corresponding to the maximum binding energy [24].

The values of the Langmuir, Freundlich and Temkin isotherms constants are grouped in the Table 01.

Table 1*. Parameters of the adsorption isotherms studied for the two types of clays.*

Isotherm model	AC-300°C	AS-300°C
Langmuir		
Q_{max} *(mg/g)*	500	238
K_L *(L/mg)*	0	0.57
R^2	1	0.9996
Freundlich		
K_F*(L/mg)*	1.095	0.051
1/n	0.172	1.517
R^2	0.45	0.806
Temkin		
B	100.8	60.32
A	31.75	1.997
R^2	0.993	0.942

The modeling of adsorption isotherms according to Langmuir data coincide with our experimental values, contrary to the Freundlich and Temkin model (Table 1). The best regressions are always obtained with the Langmuir linearization with R^2 correlation coefficients found are all close to 1 for both adsorbents, unlike the Freundlich model. Nevertheless, we can deduce that the adsorption of BM on both types of clays AC-300 ° C and AS-300 ° C also follows the model of Temkin.

The value of the capacity q_m is in good agreement with the maximum experimental value of the amount of MB adsorbed. The study of isotherms BM adsorption was carried out by Elmoubarki, et al [25] using a Moroccan clay. The results show that the Langmuir model is suitable to describe adsorption of MB compared to Freundlich's model and that of Dubinin-Radushkevich. [17]. Also showed that adsorption of MB on illitic- kaolin natural clay is better modeled by the Langmuir model than the Freundlich model.

III.7. Kinetic analysis of ortho-Cresol

In order to understand the adsorption mechanism of MB on AC-300°C and AS-300°C, kinetic models of pseudo-first order and pseudo-second order [14] were described in this present study (Figure 9 and 10).

The equations of the first and second pseudo order were used to describe the adsorption reactions, using equations Lagergren.

$$Log(q_e - q_t) = Log(q_e) - \left(\frac{K_1}{2.303}\right)t \quad \textbf{(6)}$$

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^{\,2}}\right) + \left(\frac{1}{q_e}\right)t \quad \textbf{(7)}$$

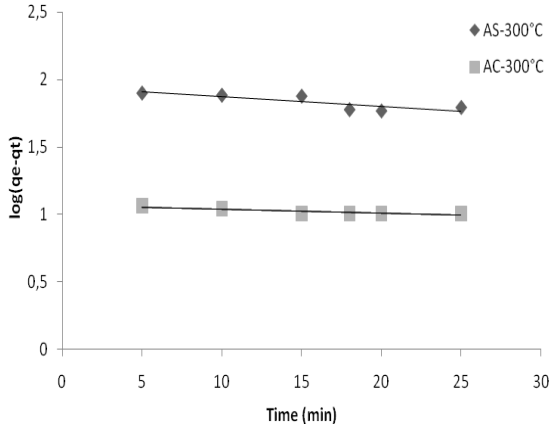

Figure 9. *Pseudo-first order for the adsorption of the methylene blue on AS-300°C and AC-300°C*

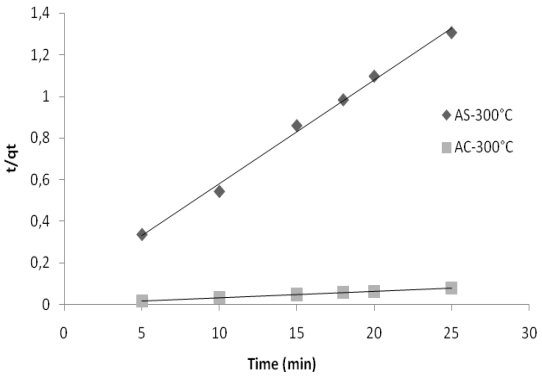

Figure 10. *Pseudo-secondorder for the adsorption of the methylene blue on AS-300°C and AC-300°C*

The obtained results from the Table 2 show the linearization of the kinetic equations gives higher correlation coefficients in the case of second-order kinetics; these coefficients may exceed 0.998 and are close to unity. This confirms that the adsorption of methylene blue onto the adsorbents (AC-300°C and AS-300°C) follows well the second-order kinetics.

Table 2. Values of the *pseudo first-order and second-order kinetic parameters*

Adsorbate			**MB**	
Pseudo-first order	qe	qe(exp)	K_1	R^2
AC-300°C	2.86	300	0.003	0.801
AS-300°C	87.29	98.58	0.013	0.709
Pseudo-second order	qe	qe(exp)	K_2	R^2
AS-300°C	105.2	98.52	$2.44\ 10^5$	0.998
AC-300°C	333.33	320	0.126	1

III.3. Thermodynamic study

The thermodynamic parameters of the MB adsorption process are calculated from the results obtained at different temperatures according to following equations [26]:

$$\ln K_d = \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{RT} \quad \textbf{(8)}$$

$$\Delta G = \Delta H_{ads} - T\Delta S_{ads} \quad \textbf{(9)}$$

The plot of Ln Kd as a function of 1/T gives a straight line whose slope allows determining the enthalpy ΔH_{ads}, the entropy ΔS_{ads} as well as the free energy ΔG_{ads}.

Table 3. *Thermodynamic parameter of MB adsorption on AC-300°C and AS-300°C.*

Adsorbate / Adsorbent	**MB AC-300°C**				
T(K)	293	308	318	328	38
ΔH (KJ.mol^{-1})	14.05				
ΔS (KJ. mol^{-1})	0.109				
T ΔS	31.9	33.5	34.6	35.7	6.8
$-\Delta G$(KJ. mol^{-1})	17.8	19.4	20.5	21.6	22.7
Adsorbate / Adsorbent	**MB AS-300°C**				
T(K)	293	308	318		328
ΔH(KJ.mol^{-1})	31.32				
ΔS(KJ.mol^{-1})	0.19				
T ΔS	56.0	58.9	62.7		64.6
$-\Delta G$(KJ.mol^{-1})	24.7	27.6	31.4		33.3

According to the results, the positive values of ΔH_{ads} imply that the adsorption process is endothermic and physical type, as found in other findings done by [27, 28]. The negative values of the free energy ΔG confirm the spontaneity of the adsorption [28].

During adsorption, the variation of entropy ΔS_{ads} is necessarily negative, the solid state is more ordered than the liquid state. Overall, it can be seen from the previous remarks that the fixation of MB on both types of clay AC-300°C and AS-300°C is an irreversible physical adsorption which is essentially distinguished by

the speed and spontaneity of the system at higher temperatures [29].

IV. Conclusion

The objective of this study is focused on the adsorption of the cationic dye (Methylene Blue) that may be present in dye waters on two local clays: the first sodium and the second calcium which are thermally activated at 300 ° C (AC-300 °C and AS-300 °C).

The adsorption results of the MB for the two adsorbents AC-300 °C and AS-300 °C show that this discoloration is influenced by several factors such as: contact time, pH of the solution, mass of the adsorbent, and temperature.

Both clays AC-300 °C and AS-300 °C gave satisfactory results; with a dye removal yield which exceeds 98%. The optimum pH for a high discoloration is pH=6.6 for both types of adsorbents.The results deduced from adsorption isotherms show that MB retention s predictable in agreement with the Langmuir and Temkin models.

The adsorption of MB on both types of adsorbents is endothermic, spontaneous and physical nature. Thermally activated clays prove to be better adsorbents in order to eliminate the dye (methylene blue) from industrial effluents.

Acknowledgments

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