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DFVELOPMENT OF NEW LOW COST MATERIALS FOR ENVIRENEMENT TRAITEMENT

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Abstract –
Water is a basic unit for the continuation of the life. But today it is seen that the ground and water pollution, accidentally or voluntarily. Various industries, such as textile, are widely ejected a large volume of colored aqueous effluents. Their presence in water has more or less serious incidences to aquatic life and also it severe damages to the human bodies. Various technologies have been developed for decontamination Adsorption process has been proven as one of the best wastewater treatment technologies around the world.
Research is centered on the use of new low cost materials, available locally, biodegradable, manufactured from natural sources. Because of their very significant structure, their great specific surface and their great capacity of adsorption, the adsorbents from clays were largely used to treat various effluents. In the present study, detailed experiments are carried out to remove brilliant green and methylene blue by adsorption technique using bentonite as an adsorbent. Based on the results obtained from the study, it appears that the acid activated clays constitute a good adsorbent for removing cationic dye.
Keywords: Pollution, water, dye, clay, bentonite, adsorption.

I. Introduction

Various industries, such as textile, leather, paper, plastic and rubber [1] are widely ejected a large volume of colored aqueous effluents. Their presence in water, even with infinitesimal quantities has more or less serious incidences to aquatic life and also it severe damages to the human bodies. [2]-[3]. So water of rejections is strongly concentrated in this toxic effluents of which the low biodeterioration makes the treatment biological not easily applicable. As a result, the removal of color from wastewaters has become environmentally important.
Various adsorbents have been explored for the removal of textile dye effluents from aqueous solutions, due to their easily preparation and regeneration, their variety of structural and surface properties, high chemical stability, high specific surface area and high adsorption capacity [4]. Congoredclayminerals One of these adsorbents, smectite clays (specially bentonite) are often employed in such operations, they have continuously attracted attention also for the possibility of modifying their layered structure by functionalization, thus creating new hybrid materials with high reactivity [5]-[6].

Various technologies have been developed for decontamination purposes including chemical oxidation, biological treatment, coagulation–flocculation, and membrane separation. [7] However, these treatment processes are costly and cannot effectively be used to treat a wide range of dye containing wastewater. Adsorption process has been proven as one of the best wastewater treatment technologies around the world. [8]-[9]
It was recognized to be a promising and a cost-effective process to remove colors from aqueous solution with the advantages of high efficiency, simple operation, and easy recovery and reuse of adsorbent.

In the present study, detailed experiments are carried out to remove brilliant green and methylene blue by adsorption technique using bentonite as an adsorbent.

II. Experimental

II.1. Materials

The materials used in the present study were a bentonite clay mineral obtained from Hammam Boughrara (West Algeria). Chemical analysis was found to be as: 69.4%

SiO2, 1.1% MgO, 14.7% Al2O3, 0.8% K2O, 0,3% CaO, 1.2% F2O3,
0.5% Na2O, 0.2% TiO2, 0.05% As, 11% loss of ignition. [10] Sodium chloride (analytical grade), sulfuric acid (H2SO4, 98wt. %), methylene blue ($C_{16}H_{18}N_3ClS$, C.I: Basic bleu 9, FW: 319,85, dye content: 99%, λmax: 665 nm), and brilliant green ($C_{27}H_{34}N_2O_4S$, C.I: 42040, FW: 462.65, dye content: 85%, λmax: 625 nm) were purchased from Sigma-Aldrich Chemicals.

II.2. Sample preparation

Sodium montmorillonite (NaMt) was prepared by treating the purified bentonite (B) with 1 M NaCl solution under mechanical stirring for 24 h at ambient temperature. This procedure was repeated three times in order to attain maximum saturation as this process gives effective saturation of sodium ions. The homoionic bentonite was dialyzed in deionized water until it was free of chloride. Then it was separated by centrifugation to eliminate all other solid phases (quartz, cristoballite). The sodium montmorillonite was recovered by decantation and dried at 80°C.
The acid activation was performed at 90 °C by mixing appropriate amounts (10 g) of purified bentonite and sodium montmorillonite with concentrated sulfuric acid (1M), the mixtures were stirred at room temperature for 6 h. After acid treatment the clay minerals were separated by centrifugation and washed rigorously with distilled water several times till it were free of $SO4^{2-}$ as indicated by the $AgNO_3$ test and were then dried at 80 °C for 24 h. Acid-activated purified bentonite (AB) and sodium montmorillonite(ANaMt) were then stored for further use in the adsorption tests.

II.3. Methods of characterization

II.3.1. FTIR analysis

Elemental analysis was performed by the Fourier Transform Infrared Spectroscopy (FTIR) using a Perkin Elmer FTIR spectrometer(Spectrum1000). FTIR spectra were measured between 4000 to 400cm−1 with KBr pellet technique. The FTIR spectroscopy was acquired to detect the changes in the structure of acid activated clay minerals and the possible formation of the three dimensional silica phases.

II.3.2. XRD analysis

X-ray diffraction (XRD) analysis was performed on the clay powders using a Bruker Advance 8 diffractometer, operating at 40 kV and 40 mA, with Cu-Kα radiation (λ=1.54 Å). The basal spacing distances (d001) were calculated from the 2θ values using the Bragg equation. The PXRD was performed to evaluate the effect of acid treatment on the structure, crystallinity of the clay mineral.

II.4. Kinetic studies

Stock solutions of dyes of concentration 1000 mg/L were prepared by dissolving 1 g of solid dye in 1L of deionized water. These solutions were diluted as required to obtain the standard solutions (50,100, 200mg/L) of MB and BG.
Adsorption experiments were carried out in a batch equilibrium mode. The effects of pH (4-10), temperature (25, 35, 45 and 55°C), initial dye concentrationC_0 (50, 100 and 200 mg/L) and adsorbent mass (10, 20, 40, 60, 80, 100, and 200 mg) were investigated by equilibrating a definite amount(0.05 g) of activated acids clays (AB and ANaMt) in 50 mL of dye solution at pH=4(brilliant green) and at pH= 7(methylene blue) for 120 min with constant shaking at 23 ± 2°C. After 2 h, the solutions attained equilibrium and the amounts of MB and BG adsorbed were derived from the initial and final concentrations of dye in the liquid phases.
The amount of dye adsorbed q_t (mg/g) and dye removal efficiency R (%) were calculated by the following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

$$R = \frac{(C_0 - C_t)V}{C_0} \times 100 \qquad (2)$$

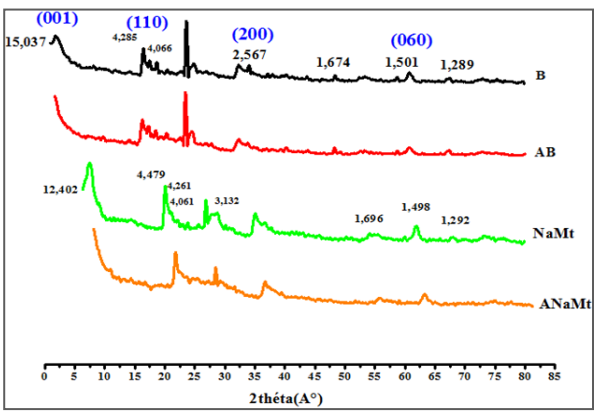
Where q_t in (mg/g) is the amount of dye adsorbed at time t, C_0 is the initial dye concentration (mg/L), C_t is the concentration of dye at any time t, V the volume of solution (L) and m is the mass of adsorbent (g).

III. Results and discussion

III.1. Characterization of adsorbents

III.1.1 FTIR analysis

During the acid treatment, many changes occurred in the aluminosilicate structure due to dissolution of structural ions and rearrangement of the structure. The FTIR spectra of acid-activated purified bentonite (AB) and sodium montmorillonite(ANaMt) are depicted in Fig.1.
The analysis of these spectra shows the principal absorption bands of the modes of vibration of the various functional groupings:
The broad band centered near 3620 cm^{-1} is due to to –OH stretching mode related to octahedral cations Al (Al-OH-Al) [11] and the band centered on 3440 cm^{-1} is due to –OH stretching mode of interlayer water.
The overlaid absorption peaks in the region of 1642 cm^{-1} is attributed to – OH bending mode of adsorbed water and the intense band observed at 1030 cm^{-1} is attributed to Si–O stretching (inplane) vibration for layered silicates.
The IR peaks at 915, 8 65, 792, 624 and 520 cm^{-1} are attributed respectively Al-OH-Al,



Si-O-Al and Al-OH-Mg, Cristobalite, Si-O-Mg and Mg-OH AlMgOH bending vibration . [12]
The intensity of the various bands have also reduces after the acid treatment or completely disappeared. This are due to the removal of octahedral cations causing the loss of water and the hydroxyl groups linked to them. This result may be an acceptable evidence for the acid activation occurring on the clay.

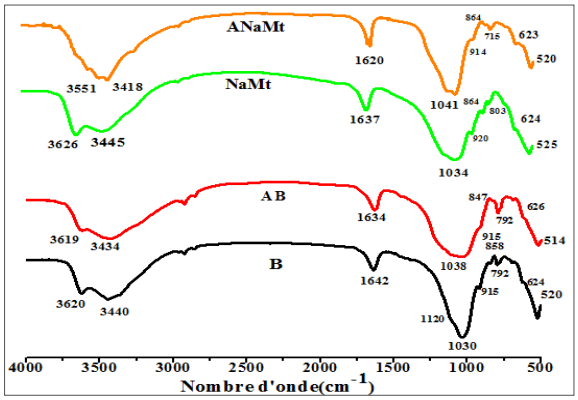


Figure.1. FTIR spectra of raw and acid activated clay.

III.1.2. Powder X-ray diffraction

The XRD powder-patterns for the raw clay and the acid-treated clay are given in Figure.2. The purified bentonite was characterized by four peaks, the first is located at 15.037 Å (**001**) and the three others are to 4. 508 Å (**110**), 2.567 Å (**200**) and 1.501 Å (**060**). The non-clay minerals present in the XRD patterns were: quartz (d $_{001}$ = 3.35 Å and 4.28 Å), calcite (d $_{001}$ = 3.21 Å), and feldspars (d $_{001}$ = 4.06 Å).
The d001 reflection of NaMt has been reduced from 15, 037 to 12, 402Å, this reduction is due to displacement of the cations Ca^{+2}, Mg^{+2}, K^{+} by the sodium ions Na^{+} that shows the homoionic validity of the exchange.
It has been observed in Fig. 1 that the acidification affects the crystalline structure of the B and NaMt. The *d*(001) values reflected a clear reduction of the distance of sheets as a result of acid sulfuric treatment. The degree of crystallinity for the raw clay was higher than that of the acid-treated clay. The raw clay is better organized than the acid-treated clay.

III.2. Adsorption studies

III.2.1.Effect of the solution pH

The effect of solution pH on the equilibrium uptake capacity of acid activated clay was studied at 100mg/L initial methylene blue and brilliant green concentration between pH value of 4 and 10. The initial pH was adjusted with NaOH or HCl solutions.
The pH PZC values for the acid activated clay studied was: B=7.9, AB=4.8, ANaMt =5.6.

Figure.2. X-ray diffraction patterns of raw and acid activated clay.

Is shown in Figure.3 that the adsorption capacity of brilliant green onto the studied clay decreased significantly when the pH of dye solution increased from 4 to 10 and the maximum adsorption of methylene blue takes place at pH value of 7.
The variation in the dye uptake with respect to the initial solution pH can be explained on the basis of the structure of dye molecule and points of zero charge (pH PZC) of acids activated clays (Figure.4)
For BA and ANaMt, the point of zero charge is estimated to be as 4.79 and 5.58 respectively. Above this pH, the clay particle acquires a negative surface charge leading to a lesser dye uptake since dye molecule becomes neutral at that pH. At a pH lower than pH PZC the clay surface acquires positive charge and dye molecules also become positive charge.
According to these explications, two possible mechanisms of the adsorption of the brilliant green and methylene blue on the acid activated clay can be considered: electrostatic interactions between the groups external of the adsorbents and the dyes and a chemical reaction enters the adsorbents and the adsorbates.

Figure.3. Effect of pH on the removal of brilliant green and methylene blue (C_0= 100 mg/L, T=23 ± 2°C, contact time 120min, m= 50 mg,V=50ml).

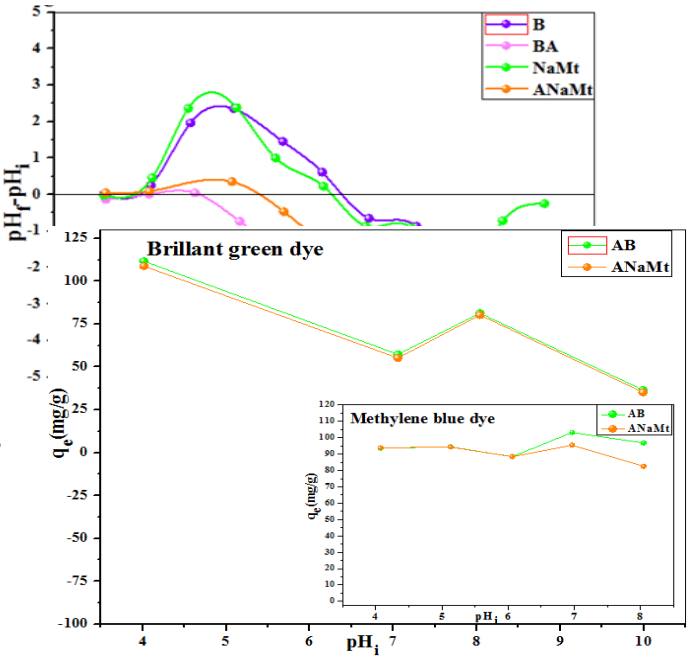


Figure.4. Points of zero charge of raw and acid activated clay.

III.2. 2.Effect of adsorbent mass

The study of the effect of adsorbent dosage gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum dosage. The adsorption of MB and BG onto AB and ANaMt was studied by changing the mass of adsorbents (10, 20, 40, 60, 80, 100, and 200 mg). It is observed from the Figure.5 that for the constant initial dye concentration (100mg/L), the increase of percentage of dye removal onto AB and ANaMt (MB: from 33.72% to 98.78% and 32.1% to 99.39% respectively and BG: from 33.72% to 98.78% and 32.1% to 99.39%) when the adsorbent dose increased from 10 to 200mg/L. This may be due to an increase in the number of active sites of the adsorbents materials with increasing amount of the adsorbents and an increase of surface area. [13]-[14]-[15]

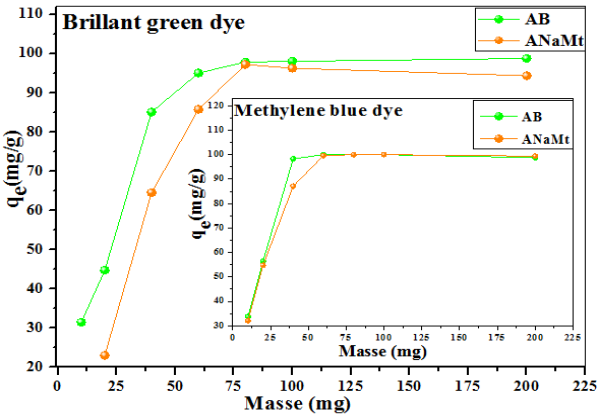


Figure.5. Effect of adsorbent dosage on the removal of brilliant green and methylene blue :(C_0=100mg/L, contact time 120min, pH_{BG}=4 pH_{MB}=7, V=50ml, T=23 ± 2°C).

III.2.3. Effect of contact time and initial dye concentration

It is seen in Fig.6 that the sorption process of methylene blue and brilliant green can be divided into three parts: the first part of the kinetics corresponding to a very short phase extending over the first 10 min and a second part of slow approach to equilibrium covering about 80 min. The third part is well represented by equilibrium stage. [16]

This phenomenon can be explained by the existence of more number of vacant sites available at the initial part localized on external surfaces from the adsorbents

The later slow rate of MB and BG adsorption probably occurred due to the electrostatic hindrance as well as the slow pore diffusion of the solute ions into the bulk of the adsorbents.

The effect of initial dyes concentration on the rate of adsorption onto acid-activated clays was investigated in Figure.4. The amount of dyes adsorbed increases with time for all initials concentrations

The amounts of MB and BG adsorbed onto AB increased from 47,009 to 138, 35 mg/g and 53, 30 to 254,76mg/g with increase in concentration dyes from 50 to 200 mg/L and the adsorption capacity onto Na-Mt increased from 48,19 to131,67and 44,41 to177,39 mg/g with an increase in the initial methyl blue and brilliant green concentrations from 50 to 200 mg/L.

This indicates that the initial dye concentrations play an important role in the adsorption capacities of of MB and BG onto Acid-activated clay.

III.2.4. Effect of temperature on the adsorption

The temperature is a major variable in the processes of adsorption, to observe the effect of this parameter on the adsorption capacity, experiments are carried out for the dye concentration of 100 mg/L and at different temperatures (25, 35, 45 and 55°C). Increasing temperature increased adsorption capacity of MB and BG onto AB and ANaMt. This implies that the adsorption is endothermic in nature.

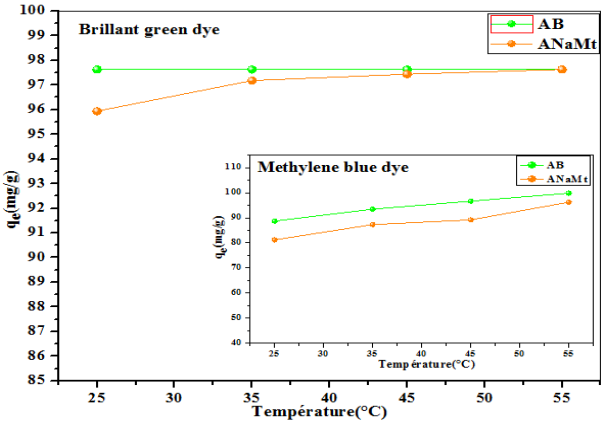


Figure.6. Effect of temperature on the removal of methylene blue and brilliant green :(C_0= 100 mg/L, contact time 120min, pH_{MB}=7, pH_{BG}=4, m=50 mg,V=50ml).

Thermodynamic parameters including change in Gibb's free energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) for the adsorption of MB and BG onto AB and ANaMt have been determined by using the Eqs (3) and (4) [17]

$$\Delta G^0_{ads} = \Delta H^0_{ads} - \Delta S^0_{ads} \qquad (3)$$

$$\log\left(\frac{q_e \times m}{C_e}\right) = \frac{\Delta S^0}{2.303 \times R} + \frac{-\Delta H^0}{2.303 \times R} \qquad (4)$$

Where *m* is the adsorbent dose (g/L), R is the universal gas constant (8.314 J/Kmol); T (K) the absolute temperature.

q_e is the amount of dye adsorbed per unit mass of clay (mg/g), C_e is equilibrium concentration (mg/L) and q_e/C_e is called the adsorption affinity.

It is observed in Table1 that for all the temperatures used, the values of ΔG^0 were all negative for the two dyes

showing that the adsorption processes on the acid-activated clay were spontaneous processes. [18]- [19]-[20]

The values of ΔH^0 were positive, which indicates that the adsorption process was endothermic and the positive values of ΔS^0 suggest the increased randomness at the solid/solution interface during the adsorption.

Table 1
Thermodynamic parameters for the adsorption of BG and MB dye on acid activated clay.

Dye		BG			MB		
	T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
AB	298	-2.3	7.1	32.10^{-3}			
	308						
	318	-2.9					
	328	-3.2					
ANaMt	298	-0.6	21.5	74.10^{-3}	-4.5	37.7	142.10^{-3}
	308	-1.3			-5.6		
	318	-2.1			-7.3		
	328	-2.8					

III.3. Kinetic models

Various kinetic models have been used to examine the controlling mechanism of adsorption of MB and BG on the surface of acid activated clay. In this study, pseudo-first-order and pseudo-second-order kinetic model are investigated to find the best fitted model for the experimental data.

III.3.1. Pseudo-first-order kinetic model

This model was developed by Lagergren (1898) for the sorption of solid/liquid systems. Its linear expression is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

Where k_1 is the equilibrium rate constant for pseudo-first-order sorption (min^{-1}), q_e and q_t are the adsorption loading of dye (mg/g) at equilibrium and at time t (min), respectively.

The slopes and intercepts of plots of ln ($q_e - q_t$) versus t were used to calculate the first-order rate constant k_1 and q_e.

III.3.2.Pseudo-second-order kinetic model

The pseudo- second -order kinetic adsorption model was suggested by Ho and McKay (1999). Is based on the assumption that the chemical sorption is the rate-limiting step and can be expressed in integrated and linear form using the following equation:

$$\frac{t}{q_t} = 1 + \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

Where k_2 is the rate constant of adsorption (g/mg min)

The plot of of t/qt versus *t is* a straight line with slope of $1/q_e$ and intercepts $1/k_2 q_e^2$. Using the value of q_e calculated from the slope, the value of k_2 is determined from the intercept.

Table 3. Kinetic parameters for the adsorption of MB onto acid activated clay.

C_o		Pseudo-first-ordre			Pseudo-seconde-ordre		
(mg/l)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$	K_1	R^2	$q_{e,cal}$	K_1	R^2
AB							
50	47.1	46.9	2.608	**0.999**	46.9	1.431	**0.999**
100	89.9	88.9	0.539	**0.990**	91.2	0.011	**0.999**
200	138.6	126.8	0.286	**0.899**	133.8	0.003	**0.956**
ANaMt							
50	48.2	47.9	1.566	**0.999**	48.2	0.231	**0.999**
100	88.5	81.2	0.240	**0.829**	87.3	0.003	**0.967**
200	131.7	115.1	0.186	**0.783**	123.8	0.002	**0.952**

Adsorption rate constants were summarized in Table2

Table 2. Kinetic parameters for the adsorption of BG onto acid activated clay.

C_o		Pseudo-first-ordre			Pseudo-seconde-ordre		
(mg/l)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$	K_1	R^2	$q_{e,cal}$	K_1	R^2
AB							
50	53.3	48.1	0.9	**0.897**	49.8	0.033	**0.936**
100	88.8	86.7	1.2	**0.993**	87.9	0.046	**0.998**
200	255.2	254.3	2.3	**0.999**	254	0.152	**0.999**
ANaMt							
50	48.1	43	0.250	**0.961**	45.2	0.009	**0.992**
100	86.7	111	0.279	**0.928**	117	0.003	**0.975**
200	254.3	163	0.241	**0.935**	173	0.002	**0.984**

and Table2, kinetic data obtained gave very good fit with the pseudo-second order model as shown by the R^2 = 0.998 values. The calculated $q_{e,cal}$

Values were very close to that of experimentally obtained $q_{e,exp}$. Thus the adsorption of methylene blue and brilliant green onto acid activated clay was explained by the pseudo-second-order kinetic model.

Similar result is found in the literature for adsorption of brilliant green adsorption onto modified kaolin and red clay. [21]

III.4. Equilibrium studies

The relationship between the adsorbed quantity on the surface of the adsorbent q_e and the equilibrium concentration of dye was studied through batch experiments by varying initial concentration of methylene blue and brilliant green.

As shown in Figure.7 that the amount of MB and BG adsorbed at equilibrium increases with an increase in initial dye concentration for the two acids activated clays. The adsorption data obtained were analyzed with the Langmuir and Freundlich isotherm equations. The best fitting isotherm was tested by determination of the linear and non linear regression, and the parameters of the isotherms have been obtained.

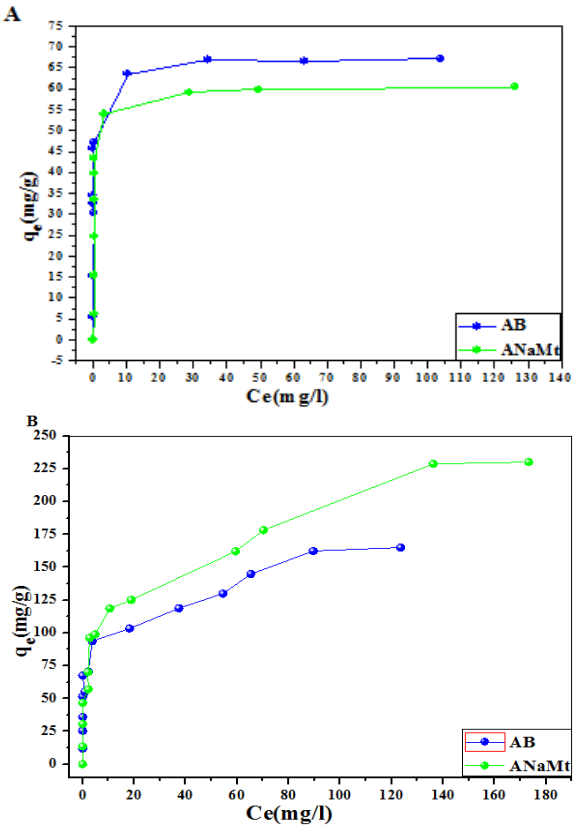


Figure.7. Adsorption isotherms of MB (A) and BG (B) of raw and acid activated clay.

III.4.1. Langmuir isotherm

The Langmuir isotherm is applicable to homogeneous sorption, where the sorption of each sorbate molecule onto the surface has equal sorption activation energy [22].

$$\frac{1}{q_{ads}} = \frac{1}{k_L q_{max}} \frac{1}{C_e} + \frac{1}{q_{max}} \qquad (7)$$

This model isotherm is expressed using the following equation: [23]

$$q_e = \frac{q_{max} k_L C_e}{1 + k_L q_{max}} \qquad (8)$$

Where q_e is the equilibrium dye concentration on adsorbent (mg/g),
C_e is the equilibrium dye concentration in solution (mg/L), q_{max} is the monolayer capacity of the adsorbent (mg/g) and k_L is the Langmuir adsorption constant (L/mg).The linear expression of this model:
Langmuir isotherm parameter for the removal of methylene blue and brilliant green onto acid activated clay can be obtained by plotting $1/q_e$ versus $1/C_e$.

III.4.2. Freundlich isotherm

The Freundlich isotherm is used for non-ideal sorption that involves heterogeneous sorption. This model isotherm is expressed using the following equation: [24]

$$q_e = k_F C_e^{1/n} \qquad (9)$$

Where q_e is the equilibrium dye concentration on adsorbent (mg/g),
C_e is the equilibrium dye concentration in solution (mg/L), k_F (mg/g) and 1/n are the Freundlich constants characteristic of the system, indicators of adsorption capacity and adsorption intensity, respectively.
Linear form of Freundlich isotherm is:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \qquad (10)$$

The values of n and k_F were calculated from the slope and the intercept of the plots of $\ln q_e$ versus $\ln C_e$
The values of the constants obtained for the two models are shown in Table4.
As seen in Table4, the Langmuir maximum capacity of BA and ANaMt was found to be 165 mg/g, 232 mg/g respectively for brilliant green and 67mg/g, 60 mg/g for methelyne blue. The values of the correlation coefficients demonstrate good agreement of the experimental data with the Langmuir model isotherm with a good correlation coefficient (**0,965** $\leq$ **R^2** $\leq$ **0,999**), which indicate the monolayer coverage onto the BG and MB particles and the homogeneous distribution of active sites on the acid activated clay. The experimental data to Freundlich's adsorption isothermal model did not lead to linearization indicating the non acceptability of isothermal model. Similar observations were reported for equilibrium studies of methelyne blue onto on a new clay class containing chitosan [25] and montmorillonite [26] and of brilliant green adsorption. [27]- [28]

IV. Conclusion

Based on the results obtained from this study, it appears that the acid activated clays constitute a good adsorbent for removing cationic dye from aqueous solution. The adsorption is highly dependent on various operating parameters, like; adsorbent dose, contact time, pH, initial dye concentration. The results showed that the amount of BG and MB uptake increased with increasing initial dye concentration, contact time, adsorbent dose and temperature.
On the other hand acid activated clays are able to absorb brilliant green and methylene blue at a very high extent of 232 mg/g and 67mg/g respectively. Materials obtained are natural, no pollutant and low cost adsorbents. We can

Table 4. Isotherm constants for the adsorption of BG and MB onto acid activated clay.

	Langmuir			Freundlich		
	q_{max}	K_L	R^2	K_F	n	R^2
BG						
AB	154	0.286	**0.970**	61	5.230	0.926
ANaMt	224	0.149	**0.980**	59	3.849	0.921
BM						
AB	75	18	**0.999**	53	9.543	0.204
ANaMt	61	0.927	**0.965**	29	3.891	0.142

conclude that it can be used for water purification and it can preserved environment.

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