BATCH ADSORPTION OF METHYLENE BLUE ON SILICA GEL OBTAINED FROM TUNISIAN SAND

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ABSTRACT : Silica gels used were obtained by alkaline attack of Tunisian sand, coming from Feriana region. A kinetic of methylene blue adsorption in liquid phase onto silica gels has been studied. The results show the effects of silica gel pH, initial concentration of methylene blue and temperature on adsorption capacity. Adsorption isotherms have been determined and fitted according to the Langmuir and Guggenheim NAnderson NDe Boer (G.A.B.) equations. A high adsorptive capacity was observed. Thermodynamic parameters such as ΔH and ΔS were determined.

Keywords: silica gel, adsorption, isotherms, kinetics, modelling.

RESUMÉ : Le gel de silice utilisé est obtenu à partir d'une attaque alcaline d'un sable Tunisien provenant de la région de Fériana. La cinétique de l'adsorption du bleu de méthylène sur les gels de silice a été étudiée. Les résultats obtenus montrent l'effet du pH du gel de silice, la concentration initiale et la température sur la capacité d'adsorption. Les isothermes d'adsorption ont été déterminées expérimentalement et modélisées selon les équations de Langmuir et de Guggenheim N Anderson N De Boer (G.A.B.). Une grande capacité d'adsorption est observée. Les paramètres thermodynamiques, ΔH et ΔS, ont été calculés.

Mots clés : gel de silice, adsorption, isotherme, cinétique, modélisation.

1. INTRODUCTION

In industrial water pollution, the colour produced by minute amounts of organic dyes in water is considered very important because, besides having possible harmful effects, the colour in water is aesthetically unpleasant [1].

In recent years adsorption systems using activated carbon have been widely employed in the purification of water and wastewater [2,3]. The contacting systems include batch, fixed bed and fluidised bed adsorbers [4-6]. Several small scale adsorption studies have been undertaken using other adsorbents [7-9].

The silica gel was used as adsorbent of humidity (dehydration of air, purification of gases) or as important adsorbent in liquid phase. The ability of silica gel to adsorb dyes from aqueous solution in the various contacting systems has been reported [10,11].

The adsorption of methylene blue in liquid phase is usually used to determinate specific surface area of various natural solids: activated carbon, graphite, clay and silica gel, for example [8,11-13]. In order to understand the mechanism of dye adsorption onto silica gel, we performed simulation experiments using methylene blue as a model solution.

The objective of this paper is to enhance adsorbent properties of silica gel prepared from Tunisian sand. A kinetic study of methylene blue adsorption onto silica gel was first conducted to establish the adsorption isotherms. The results were fitted by the famous Langmuir and Guggenheim N Anderson N De Boer (G.A.B.) models. Also, the thermodynamic parameters such as heat adsorption and entropy adsorption were evaluated.

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2. MATERIALS AND METHODS

2.1. Silica gel and methylene blue solution

2.1.1. Silica gel

Silica gel used is prepared in the laboratory from Tunisian sand recuperated from Feriana region (Kasserine). The preparation of silica gel needs two successive stages:

- Alkaline attack of the sand driving to a silicate

$$n\,SiO_2 + 2\,(NaOH, xH_2O) \longrightarrow nSiO_2, NaO, yH_2O \quad (1)$$

- Destabilization of the silicate by acid attack

$$\underset{\text{Silicate}}{Na_2SiO_3} + 2\,(H_3O^+ + Cl^-) \longrightarrow Si(OH)_4 + 2\,NaCl + H_2O \quad (2)$$

$$\underset{\text{Silicic acid, ortho}}{2\,Si(OH)_4} \xrightarrow{-\,H_2O} \underset{\text{Disilicic acid}}{(HO)_3Si\text{-}O\text{-}Si(OH)_3} \xrightarrow{-n\,H_2O} \text{Silica gel} \quad (3)$$

The destabilization of a colloidal solution by hydrochloric acid, transforms silicate ions to many silicic acid, which by poly-condensation led to hydrated porous silica gel [14]. Adsorption performance of silica gel depends on many factors like temperature, HCl concentration and silica gel pH. Silica gel is washed with distilled water, in order to eliminate chlorides.

For adsorption study, the silica gel is used under grain form. Particle diameter is less than 63 µm. The chemical composition of oxides included in the used silica gel (SG6), is presented in Table I.

Table I : Chemical composition of silica gel (SG6) (wt. %)

Constituent	SiO_2	Na_20	K_2O	Fe_2O_3	Al_2O_3	Cl^-	P.F*
Wt (%)	36.68	7.03	0.013	0.004	0.002	0.51	55.7

*Ignition loss

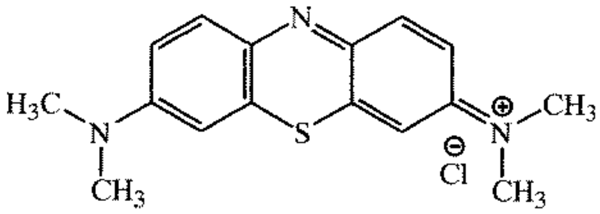
The textural analysis of silica gel is presented in Table II.

Table II : Textural composition of silica gel (SG6)

Real volumetric mass, ρ_s	$\rho_s = 2.28$ g.cm^{-3}
Apparent volumetric mass, ρ_p	$\rho_p = 0.56$ g.cm^{-3}
Porosity, χ	$\chi = 75$ %
Porous volume, V_p	$V_p = 1.34$ cm^3.g^{-1}
Specific surface area, $S_{B.E.T}$	$S_{B.E.T} = 548.8$ m^2·g^{-1}
Middle radius pore, $<r_p>$	$<r_p> = 4.88$ nm

2.1.2. Methylene blue solution

Adsorption studies used methylene blue (MB) or 3,7-bis-(dimmethylamino)-phenothiazin-5-ium ion ($C_{16}H_{18}ClN_3S$, Merck product) onto silica gel. MB was chosen in this study because of its strong adsorption onto solids (clay, silica gel, activated carbon, etc.) and its recognised usefulness in characterizing adsorptive materials. Methylene blue has a molecular weight of 373.9 g mol^{-1} [15].



3,7-bis-(dimethylamino)-phenothiazin-5-ium
(Methylene blue)

Figure 1 : Methylene blue formula

2.2. Experimental procedures

Adsorption of MB was carried out in a batch process by varying silica gel pH, adsorptive concentration and temperature. A weighted sample of silica gel (1g) was mixed with 100 mL methylene blue solution of known concentration. The mixture, in a 250 mL conical flask, was shaken in the water bath of a thermostat at a particular temperature. The concentration of dye in the samples is measured by spectrophotometer (Hitachi model U-2000) at the wave-length corresponding to maximum absorbency, namely (λ_{max} = 664 nm).

A calibration curve of optical densities (OD) against MB concentrations (C) is obtained by using MB solutions of known concentrations. It has for equation:

$$OD = 0.20664 \times C \tag{4}$$

2.3. Adsorption isotherm

Many models have been developed and studied for the prediction of the relation between equilibrium liquid-solid interfaces [16-19]. These models can be theoretical, semi‐theoretical or empirical.

2.3.1. Langmuir Isotherm:

The Langmuir model is used to estimate the concentration of MB on the silica gel monolayer.

$$Q = \frac{K \cdot S \cdot C_e}{1 + K \cdot C_e} \tag{5}$$

where Q is the concentration of MB in the silica gel (mg.g^{-1}), C_e is concentration of MB in solution at equilibrium (mg.L^{-1}), K and S Langmuir constants.

Equation (5) can be linearized to give:

$$\frac{C_e}{Q} = \frac{1}{S} C_e + \frac{1}{K \cdot S} \tag{6}$$

The plot of $\frac{C_e}{Q}$ versus C_e gives a straight line with slope equal to $\frac{1}{S}$, and intercept equal to $\frac{1}{K \cdot S}$. Therefore, the Langmuir isotherm is an adequate description of the adsorption of the methylene blue onto silica gel.

Another factor, R_L, which is considered as a more reliable indicator of adsorption [20] was computed from:

$$R_L = \frac{1}{1 + K \cdot C_0} \tag{7}$$

where K is Langmuir's constant and C_0 is any adsorbate concentration at which the adsorption is carried out.

$0 < R_L < 1$, favourable adsorption ;
$R_L > 1$, unfavourable adsorption ;
$R_L = 1$, equilibrium is linear ;
$R_L = 0$, irreversible equilibrium.

2.3.2. Guggenheim – Anderson – De Boer (G.A.B.) Isotherm:

Following the literature [21,22], the GAB model is often used to describe the sorption isotherms. The general expression of this model is:

$$Q = \frac{Q_m \cdot C \cdot K_1 \cdot C_e}{(1 - K_1 \cdot C_e)(1 - K_1 \cdot C_e + C \cdot K_1 \cdot C_e)} \tag{8}$$

where Q is the concentration of MB in the silica gel ($mg.g^{-1}$), C_e is concentration of MB in solution at equilibrium ($mg.L^{-1}$), Q_m , K_1 and C are three constants to be determined. The GAB model does not simply contain the three apparent parameters but also the temperature through dependence of these parameters.

2.4. Thermodynamic parameters

2.4.1. Adsorption enthalpy

The differential heat of adsorption is the amount of energy associated with the adsorption process. This parameter is used to indicate the state of absorbed MB by the solid particles. Differential heat of adsorption is commonly estimated by applying Clausius-Clapeyron equation to adsorption isotherms. This equation is given by [23,24]:

$$\frac{d(\ell n C_e)}{dT} = -\frac{\Delta H_{ads}}{RT^2} \tag{9}$$

Integration of equation (9):

$$\ell n C_e = \frac{\Delta H_{ads}}{RT} + Cte \tag{10}$$

where ΔH_{ads} is heat of adsorption ($kJ.mol^{-1}$), C_e is the concentration of MB in solution at equilibrium ($mg.g^{-1}$).

The enthalpy ΔH_{ads} is obtained from the slope of the straight line plot of $\ell n C_e$ versus $1/T$.

2.4.2. Adsorption entropy

Integral entropy describes the degree of disorder, randomness of motion and other statistical approaches related to MB adsorption. Integral enthalpy is needed to determine integral entropy associated with the adsorption process. The adsorption entropy is determined from the following equation [25-28]:

$$\Delta S = \frac{\Delta H_{ads}}{T} - R \cdot \ell n C_e \tag{11}$$

where ΔS is the adsorption entropy ($kJ.mol^{-1}.K^{-1}$).

Integral enthalpy and entropy have been used to explain modes of MB adsorption. Generally, the entropy evolution is similar to the enthalpy.

2.4.3. Free energy

The free energy is obtained from the following equation:

$$\Delta G = \Delta H_{ads} - T \cdot \Delta S \tag{12}$$

where ΔG is the free energy ($kJ.mol^{-1}$).

Free energy is useful in calculating energy consumption during the adsorption phenomenon and in describing any heat and mass transfer related processes. The negative values of free energy indicate that the adsorption is a spontaneous phenomenon.

3. RESULTS AND DISCUSSIONS

3.1. Kinetic study

In order to determine the adsorption isotherm of MB on silica gel, an adsorption kinetic study was conducted first.

3.1.1. Effect of silica gel pH

Kinetic study was realized on many silica gel prepared at different pH (4 N 9). All the kinetic curves are obtained at the temperature of 25°C. The MB concentration is fixed for all experiments equal $C_0 = 250$ mg.L^{-1}.

After few minutes, every kinetic curve (figure 1) reaches a plateau: the MB adsorption on a silica gel is at its maximum capacity.

Figure 2 describes the maximum adsorbed quantity of MB for many silica gel prepared at different pH. The silica gel prepared at pH = 6 (SG6) is the best MB adsorhent, because it has the maximum capacity of adsorption. That is why it is chosen for the following study.

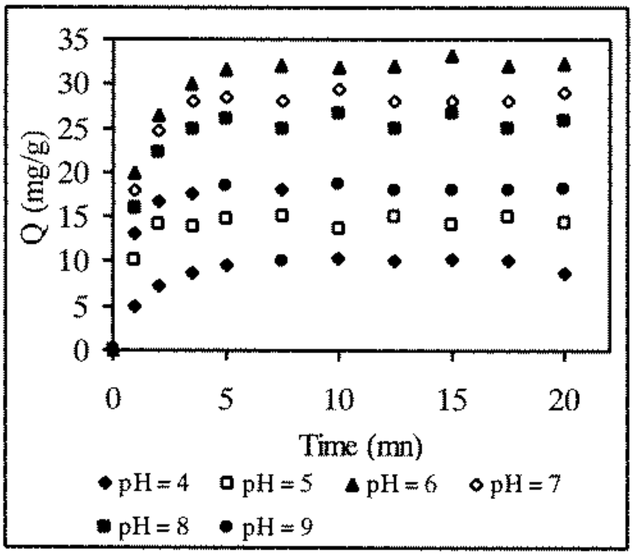


Figure 1 : Effect of silica gel pH on MB adsorption kinetic (T = 25°C, $C_0 = 250$ mg.L^{-1})

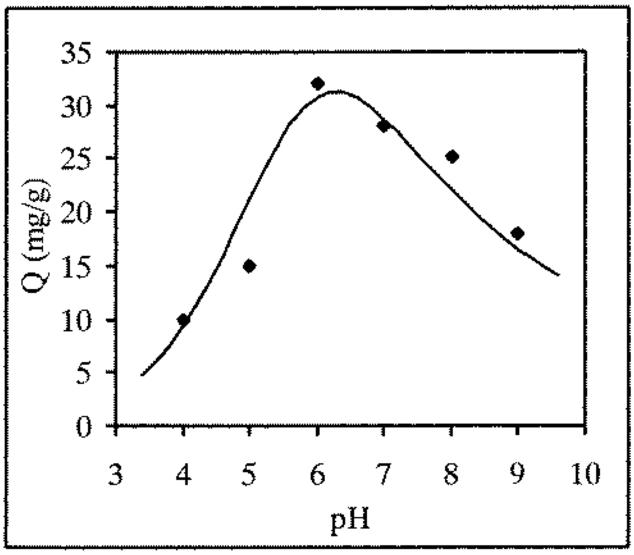


Figure 2 : Effect of silica gel pH on maximum MB adsorption capacity (T = 25°C, $C_0 = 250$ mg.L^{-1})

3.1.2. Effect of methylene blue concentration

It is in general admitted that the diffusion in the solid obeys to the three following stages:

- the external matter transfer: it is the diffusion of the adsorbate through the layer limits;
- the internal matter transfer: it is the combination of two phenomena that happen in parallel, on one hand the internal molecules transportation of the adsorbate through the pores of the adsorbent, and on the other hand, the migration of the molecules of adsorbate along the surface of the adsorbent;
- the adsorption cleanly settled.

The slowest of these three stages that is going to impose its kinetic to the global speed of adsorption.

The variation of initial MB concentration (C_0) is studied at the temperature of 25°C. Figures 3 and 4 show the effect of initial MB concentration on silica gel adsorption. Initially, the adsorption is fast. During this period, the adsorption is controlled by extra-granular mass transfer through liquid film. After 5 minutes, the kinetic of adsorption decreases. This speed decrease can be explained by a second diffusion mechanism: intra-granular mass transfer. The necessary time needed to reach the equilibrium depends on initial MB concentration [29,30]. Indeed the methylene blue molecule has a minimum molecular cross-section of about 0.8 nm, and it has been estimated that the minimum pore diameter it can enter is 1.3 nm [31]. Therefore, it can only enter the largest micropores, but most of it is likely to be adsorbed in mesopores ($\Phi > 3.7$ nm) [32]. Thus, 90 % of the adsorption capacity can be reached with extra-granular mass transfer. The methylene blue test can be used to predict organic compound adsorption (microcystin, olive waste, color bodies, etc.).

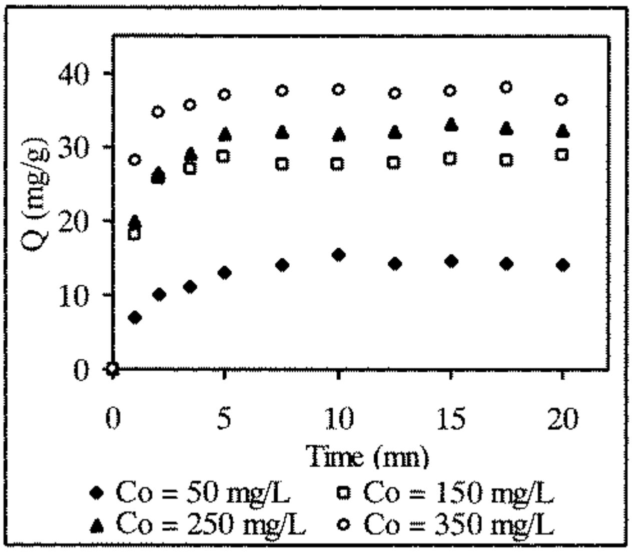


Figure 3 : Effect of initial MB concentration on adsorption kinetic on (SG6) at T = 25°C

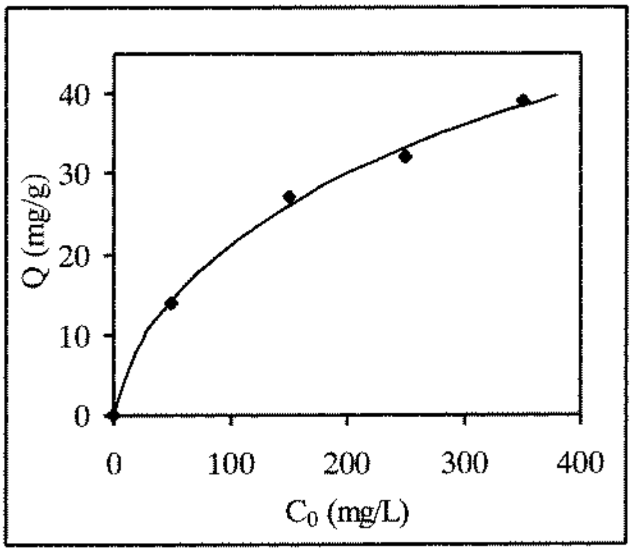


Figure 4 : Effect of initial MB concentration on maximum MB adsorption capacity on (SG6) at T = 25°C

3.1.3. Effect of temperature

Figure 5 represents the effect of the temperature on MB adsorption kinetic on (SG6). The MB concentration is fixed at C_0 = 250 mg.L^{-1}. The different curves show that the adsorption capacity increases when the temperature decreases. This phenomenon can be explained by the exothermicity of the adsorption [7].

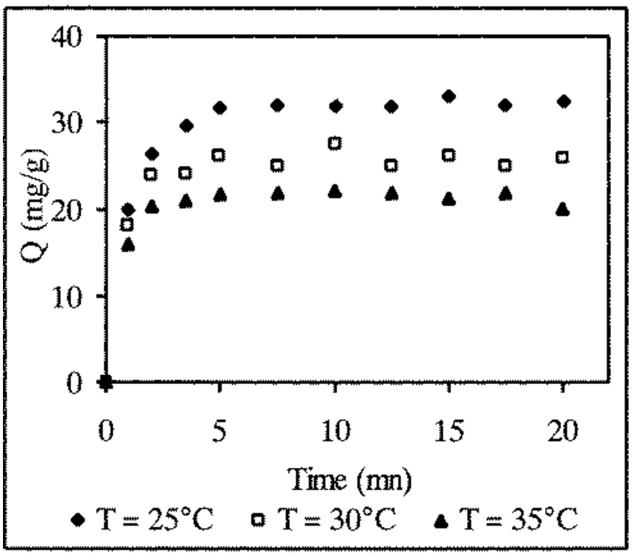


Figure 5 : Effect of temperature on MB adsorption kinetic on (SG6) with C_0 = 250 mg.L^{-1}

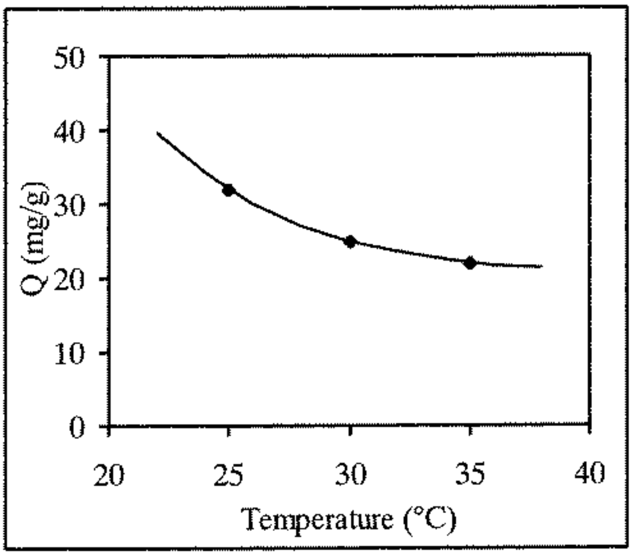


Figure 6 : Effect of temperature on maximum MB adsorption capacity on (SG6) with C_0 = 250 mg.L^{-1}

3.2. Equilibrium studies

3.2.1. Determination of adsorption Isotherms

The MB adsorption isotherms on (SG6) are carried out for many temperature (25, 30, 35 and 40°C). The experimental points can be described by the Langmuir and also GAB equations (Figures 7 and 8, Table III). The theoretical plots show that both models are in agreement with experimental results.

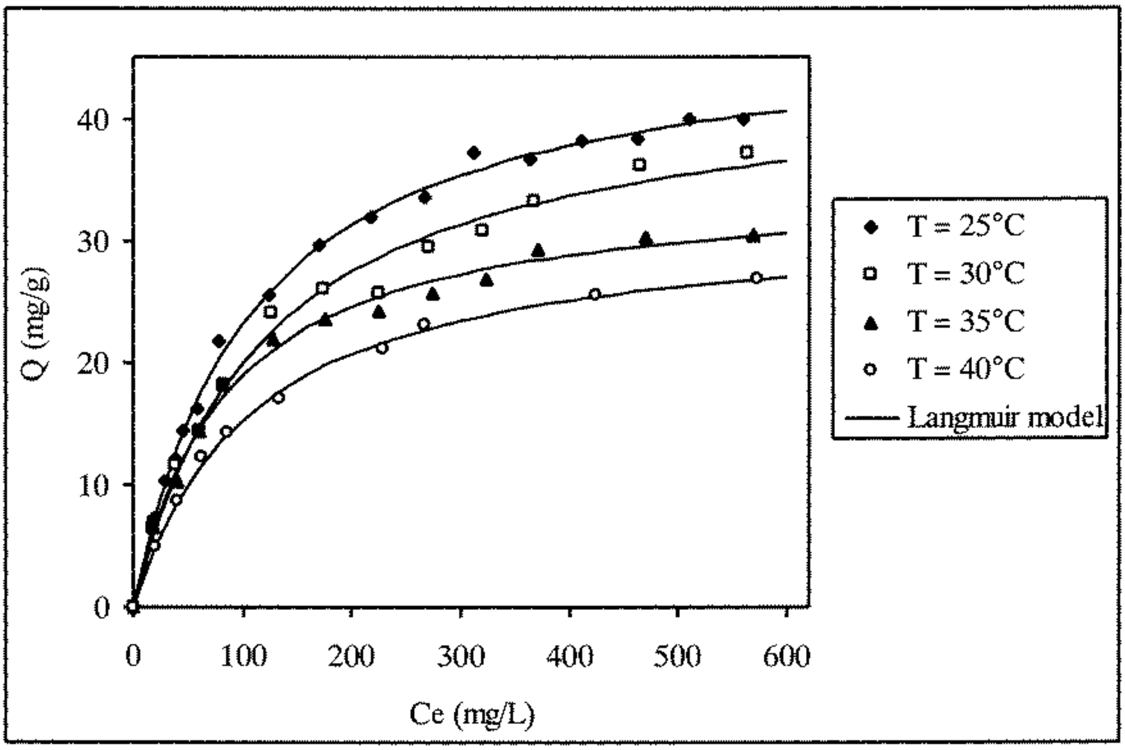


Figure 7 : Adsorption isotherms of MB on silica gel (SG6) at different temperatures fitted with Langmuir model

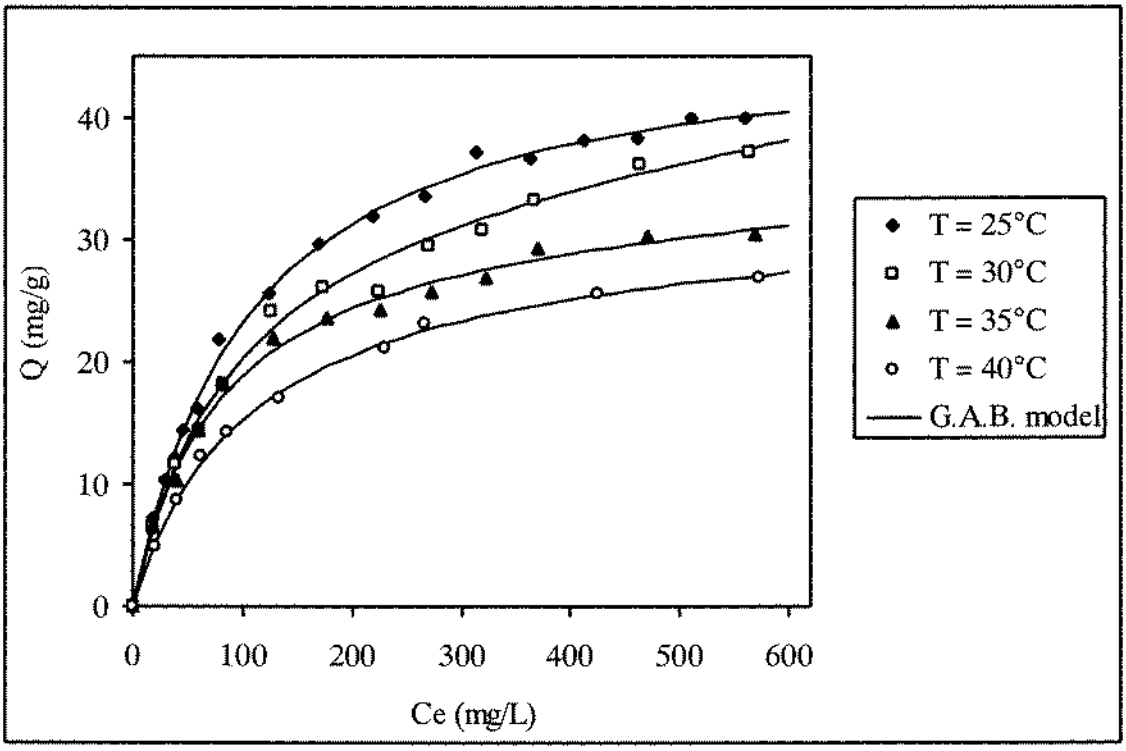


Figure 8 : Adsorption isotherms of MB on silica gel (SG6) at different temperatures fitted with G.A.B. model

According to BET classification [33], the adsorption isotherms obtained have the type I. This type is generally observed for micro porous adsorbents (activated carbon, silica gel, molecular sieve, etc.), where the adsorption is limited to one or two layers. The affinity of silica gel for MB may be ascribed to:

- Great specific area of silica gel;
- MB mobility in liquid phase and in solid micro porous;
- Interaction forces (Van der Waals) between MB molecules and adsorbent.

The isotherms show that the amount of MB adsorbed increases as the concentration increases up to a saturation point. Moreover, the adsorption capacity increases when the temperature decreases. This can be explained by the exothermicity of the adsorption reaction.

The curves Ce versus $\frac{C_e}{Q}$ (figure 9) have linear form. Then, adsorption phenomenon can be described by Langmuir model, which parameters are shown in table III.

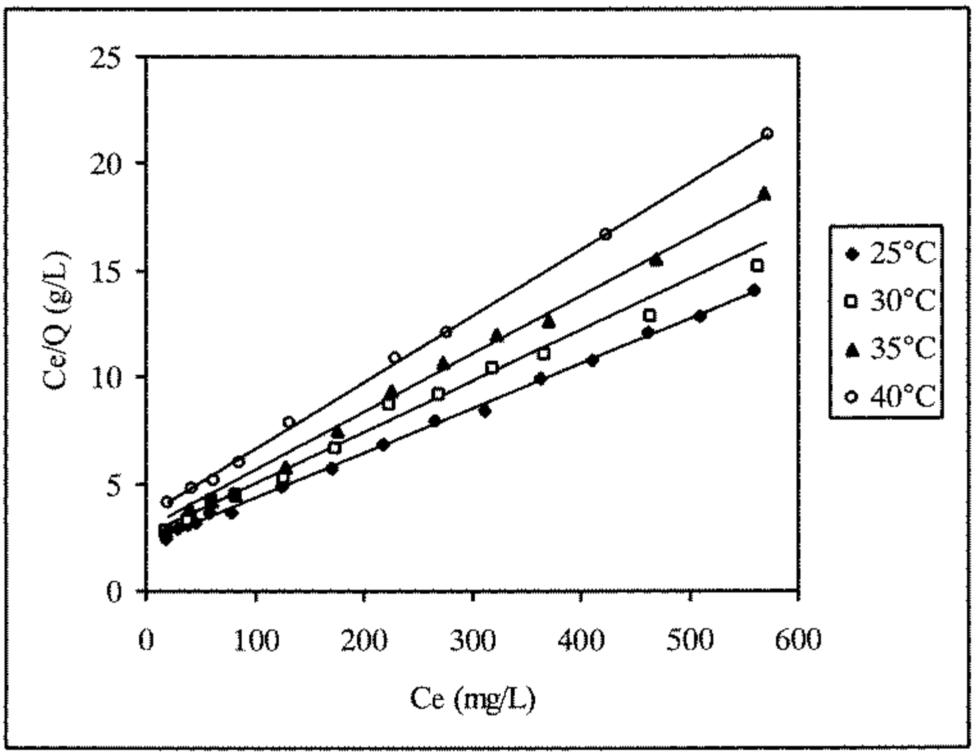


Figure 9 : Linearized Langmuir plot for MB adsorption

For Langmuir constants, K depends on adsorption temperature, adsorption enthalpy and adsorbent-adsorbat system ($L.mg^{-1}$) and S is the maximal adsorption capacity ($mg.g^{-1}$). They decrease when the temperature increases.

The influence of isotherm shape on whether adsorption is "favourable" or "unfavourable" has been considered. For the Langmuir-type adsorption process, the isotherm shape can be classified by the separation factor R_L. It is usually used in chemical engineering for the design of industrial absorbers [20]. Values of $R_L < 1$ (table III), calculated for C_0 = 20 $mg.L^{-1}$, represent favourable adsorption.

For G.A.B. constants, K_1 is the difference of activation energy in multi-layers ($J.mol^{-1}$), C is the energy excess ($J.mol^{-1}$) and Q_m is the adsorbed MB content in multi-layer's.

Table III : Langmuir and G.A.B. constants for MB adsorption on silica gel (SG6) at different temperatures

	Langmuir			G.A.B.		
	S (mg.g^{-1})	K (L.mg^{-1})	R_L	Q_m	C (J.mol^{-1})	K_I (J.mol^{-1})
25°C	47.847	9.426×10^{-3}	0.841	-48.844	0.997	-9.163×10^{-3}
30°C	44.248	9.380×10^{-3}	0.842	-36.493	1.022	-11.326×10^{-3}
35°C	35.211	9.339×10^{-3}	0.843	-32.535	1.008	-13.243×10^{-3}
40°C	31.153	9.308×10^{-3}	0.843	-30.170	1.008	-10.040×10^{-3}

3.2.2. Enthalpy and entropy of adsorption

Employing the Clausius-Clapeyron equation, the isosteric heats in the range of temperatures employed can be estimated with equation 10. A typical ℓnC_e versus $\frac{1}{T}$ plot is shown in Figure 10. The adsorption heats are presented in table IV. The values demonstrate a spontaneous and favourable adsorption. The enthalpy (ΔH) change for the adsorption process is negative, indicating that the process is exothermic in nature. The adsorption enthalpy increases when the concentration of MB in the silica gel increases.

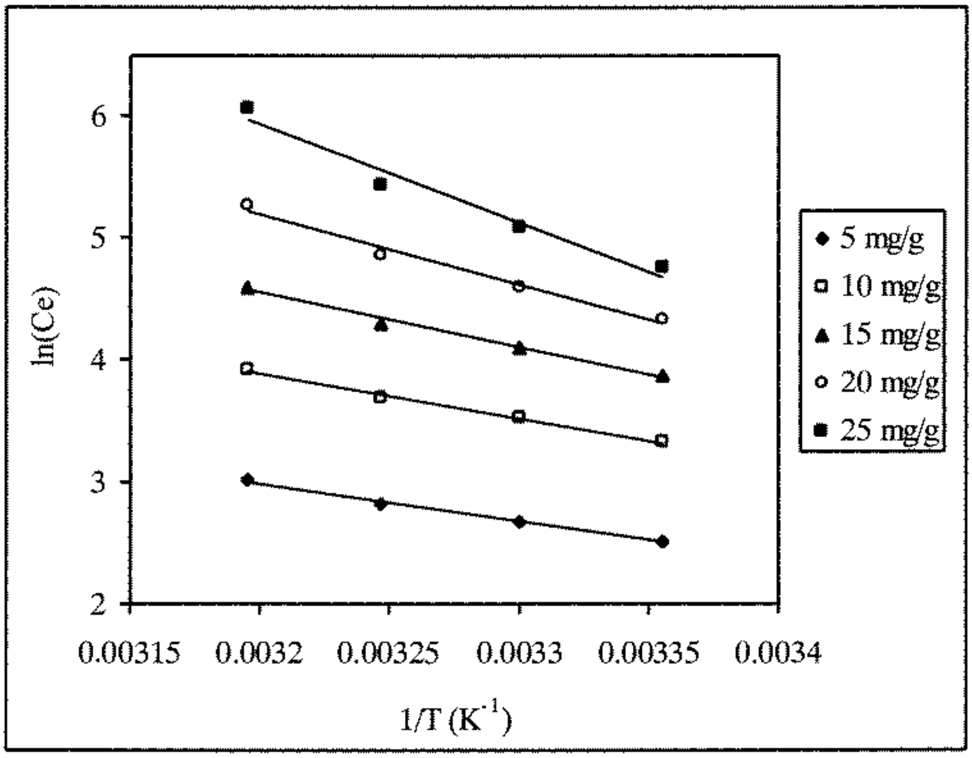


Figure 10 : Adsorption isoster of MB on silica gel (SG6)

The adsorption entropy is plotted as a function of 1/T content in figure 12. The values of entropy are not very large and indicate an increase due to adsorption. During the adsorption process, MB molecules pass from disordered state (liquid phase) to more ordered state (adsorbed phase), witch explains the negative values of entropy (table IV).

The negative values of Gibbs energy (ΔG) indicate that the adsorption of MB on silica gel is a spontaneous phenomenon and do not require a large activation energy.

Table IV : Thermodynamic parameters for adsorption of MB on silica gel (SG6)

Q ($mg.g^{-1}$)	- ΔH_{ads} ($kJ.mol^{-1}$)	- ΔS ($J.mol^{-1}.K^{-1}$) at 25°C	- ΔG ($kJ.mol^{-1}$) at 25°C
5	25.850	107.66	57.933
10	30.310	129.43	68.879
15	36.774	155.67	83.163
20	47.095	194.07	104.927
25	66.858	263.88	145.495

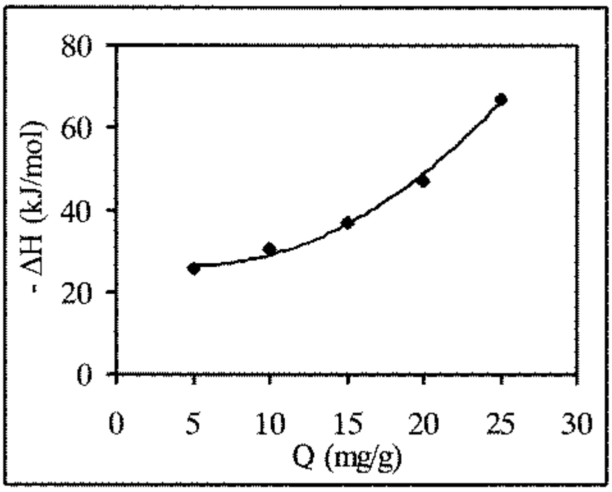


Figure 11 : Adsorption enthalpy of MB on silica gel (SG6)

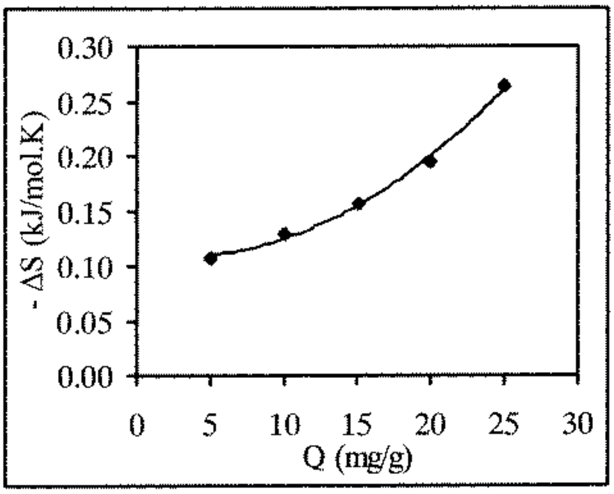


Figure 12 : Adsorption entropy of MB on silica gel (SG6) at T = 25°C

4. CONCLUSION

The silica gels prepared from Tunisian sand have good properties for adsorption. Methylene blue is used as adsorbat. The kinetic survey of adsorption onto silica gel prepared at different pH, allowed us to orient our choice on the gel obtained at pH = 6 (SG6), since it presents the best adsorption capacity in the kinetic curve. The different equilibrium curves show that the adsorption capacity increases when the temperature decreases. This phenomenon can be explained by the exothermicity of the adsorption reaction. According to BET classification, the adsorption isotherms obtained have the type I. The adsorption is limited to one or two layers.

The adsorption isotherms of MB onto silica gel are determined experimentally at different temperatures, then Langmuir and G.A.B. models are used to smooth experimental data. Isotherms show that the amount of MB adsorbed increases as the concentration increases up to a saturation point. The adsorption free energy is negative indicating that the process is spontaneous and favourable adsorption.

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