Journal of Materials and Environmental Science
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2020, Volume 11, Issue 7, Page 1044-1057

http://www.jmaterenvironsci.com

Adsorption of Methylene Blue on silica gel derived from Algerian siliceous by- product of kaolin

D. Ingrachen-Brahmi [1], H. Belkacemi [1], L. Ait Brahem-Mahtout [1]

[1] *Technology Laboratory of Materials and Process Engineering (LTMGP), University of Bejaia, 06000 Bejaia, Algeria*

Received 19 May 2020,
Revised 10 June 2020,
Accepted 11 June 2020

Keywords
- ✓ adsorption,
- ✓ silica gel,
- ✓ methylene blue,
- ✓ cationic dye,
- ✓ Siliceous by-product.

ingrachen.da@gmail.com

Abstract

In this paper adsorptive removal of hazardous dye methylene blue from aqueous solutions was investigated using the silica gel synthesized from Algerian siliceous by products (sand) collected from tamazert ore (North- East of Algeria). The prepared silica gel exhibited pore diameters exceeding 17Å and surface areas up to 477 m^2 /g, N_2 adsorption isotherms showed that the silica gels pH 2 prepared from Algerian sands are mesoporous materials with high adsorption capacities. To understand better their adsorbent properties and applicability on an industrial scale, this gel was tested for methylene blue (MB) absorption. Maximum decolorization rates (up to 80% after a contact time of 180 min). The adsorption process was pH-dependent with a high adsorption capacity at pH 5. The experimental isothermdata were analyzed using the Langmuir and Freundlich models. The equilibrium data fit well the Langmuir isotherm, revealing a monolayer coverage process of MB molecules over the gel surface, and the adsorption kinetics of the dye on these materials is well described by the second order model. The results obtained in this study show that the silica gel obtained from the Algerian siliceous by-products of kaolin could be used as an effective and low-cost absorbent material for organic pollutants, and thus represent a promising alternative for eliminating dyes from industrial wastewaters.

1. Introduction

Silica gel is an interesting amorphous material with a high adsorption capacity [1], and is used as an adsorbent of humidity, or as important adsorbent in liquid phase. Silica gel is also chemically inert and with low toxicity, with a very high melting point, it is very much like quartz sand and thus can safely be sent by any means of transport, has a long life, and has low abrasion (the wear rates decreasing with increasing of the porosity). In recent years, new studies are underway into the use of this versatile amorphous material as fillers [2], coatings [3] electronics [4] and pharmaceutical products. Silica gel exhibits superior adsorption and high surface area properties which paves its way for use in water filtration. The ability of silica gel to adsorb dyes from aqueous solution in the various contacting systems has been reported [5]

Dyes are widely used as one of the key ingredients in many industries like textile, paint and varnish etc…. These industries discharged the dye in the environment with their wastewater, and one of the major problems concerning textile wastewater is the highly colored effluent, which can be difficult to decolorize. The main environmental concern with dyes is their absorption and reflection of sunlight entering the water and thus causing reduction in photosynthesis [6].

In addition, the main concern is that some dyes degrade into compounds that have toxic, mutagenic and carcinogenic effect on living organism. Azo dyes can be particularly toxic upon degradation and this class of dyes is widely used in many industries such as methylene blue ($C_{16}H_{18}ClN_3S$). Therefore, the

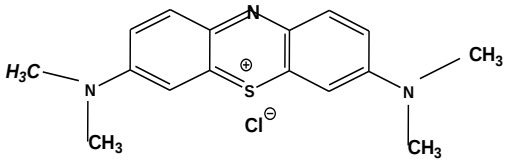
treatment of effluent containing such dye is interest due to its harmful impact on receiving water. Among various treatment methods available for dye removal, the adsorption has been proved to be the most suitable and promising technologies or has become the most popular technique because of its effectiveness, operational simplicity, low cost and low energy requirement [7]. Removal of dyes in aqueous solutions by adsorption on various solid materials, especially on silica gel, has been the subject of many studies. Many adsorbents have been tested for the removal of methylenblue from water and wastewater. Examples of these adsorbent are Fly Ash-based Geopolymer [8], silica gel from Tunisian sands [5], clay [9], activated carbon [10] and wood ashes [11].

The objective of this present work is to study the potential of silica gel from Algerian siliceous by products of kaolin for the removal of methylene blue dye (MB) from aqueous solution. To accomplish this, equilibrium and kinetic study were performed. Parameters afecting the adsorption process such as pH and temperature were also considered.

2. Material and Methods

*2.*1. Materials

Siliceous by-product of kaolin (sand) designated GOO, was obtained from Tamazert ore (North- East of Algeria). The dye used as adsorbate in the present study is the cationic dye - Methylene blue (MB)-was purchased from Sigma-Aldrich. The MB molecular structure is displayed in Scheme 1.



scheme1. Chemical structure of methylene blue

MB is a cationic dye which ionizes as shown below:

$$MB\text{-}Cl_{(aq)} \rightarrow MB^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Its visible Spectrum is shown in figure 1.

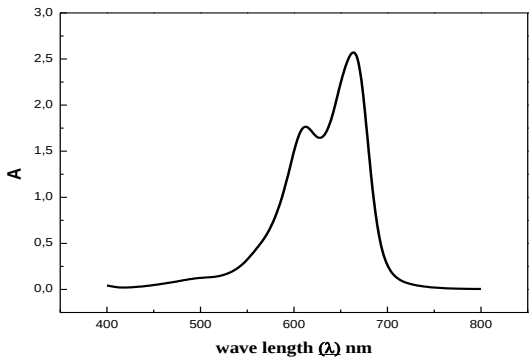


Figure 1. visible spectrum of methylene blue dye (100mg/L)

2.2. Silica gel preparation

The preparation of silica gel from treated siliceous byproduct of kaolin (sand GOO) was described in our previous work [12]. Briefly, silica gel was made in two steps: (1) the preparation of metasilicate sol and (2) the destabilization of metasilicate with dropwise addition of 2M hydrochloric acid solution until

the desired pH (pH =2). Silicate was prepared by heating a mixture of sodium carbonate and sand (GOO) at 1000 °C, a vitreous compound was produced. The sodium silicate used in this study was prepared with different molar ratios n= SiO_2/Na_2O. This ratio was varied from n=1 up to 4 to define its optimal value, which is found for n = 3. This result is close to 3.3:1 set by Hwang et al. (2007) [13].

2.3. Adsorption tests

The adsorption tests were performed for the system adsorbate (methylene blue)-adsorbent (silica gel prepared at pH 2) to define the optimal operating conditions of the main parameters related to the adsorption process. The adsorption tests were carried out in a batch reactor with suspensions of various adsorbent solid/liquid adsorbate ratios under magnetic agitation. The reactor was immersed in a water bath to stabilize the temperature.

The study of adsorption tests was performed in batch with varying contact time, initial MB dye concentration (20 to 100 mg/L), temperature (25, 35, 45, 40, 55, 65 °C) and pH MB solution (from 2 to 10). Preliminary trials were carried out by introducing 0.1 g of adsorbent (silica gel) in 100 mL of dye solution. The solutions were vigorously mixed by mechanical stirrer in the dark. Volumes (3 mL) were taken out of the solution for different time intervals, centrifuged at a speed of 5000 trs/ min during 3 min.

The absorbance of the supernatant solution was measured using a spectrometer [SCHIMADZU type UV-1800] at the wavelength that corresponds to the maximum absorbance of the sample (λ=664nm). The concentration of residual dye was calculated using the calibration curve whose equation is given by:

$$C_{dye} = 0.000526 * A_{664} + 0.21729 \qquad (1)$$

The adsorption capacity at time t, q_t (mg/g), was obtained as follows: [14]:

$$q_t = \frac{(C_i - C_t)}{m} * V * 10^{-3} \qquad (2)$$

Where q_t (mg/g) is the quantity of the dye adsorbed per unit of mass of adsorbent, C_i (mg/L) is the initial concentration of dye, C_t (mg/L) is the residual concentration of dye at the time **t**, V (mL) is the total volume of the solution, and m (g) is the mass of the adsorbent.

2.3. Adsorption Isotherms

Adsorption isotherms were used to describe the mechanism of the interaction of MB on the adsorbent surface. Two models have been adopted in this research, namely Langmuir [15] and Freundlich [16].

Langmuir isotherm model is known as idealized monolayer model. The basic assumptions of Langmuir model (i) a fixed number of accessible sites having equal energy (homogenous surface) and (ii) reversibility of the adsorption process. When the rate of adsorption becomes equal to the rate of desorption of molecules from the surface, equilibrium is reached. The form of Langmuir isotherm [11] can be given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (3)$$

Where q_m (mg/g) is the maximum capacity of adsorption; q_e (mg/g) is the capacity at adsorption equilibrium; K_L (L/mg) is the Langmuir constant. These values of K_L and q_m are obtained, respectively, starting from the intersection with the ordinate in the beginning and the slope of the right-hand side: Ce/qe = f (Ce)

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the adsorbent surface and the exponential distribution of sites and their energies. The expression for Freundlich [14] model is:

$$q_e = K_f C_E^{\frac{1}{n}} \quad (4)$$

The linear form of frundlich model [11] is:

$$Lnq_e = LnK_F + \frac{1}{n} LnC_e \quad (5)$$

Were K_F is the Freundlich constant and 1/n is the intensity of adsorption. 1/*n* is identifying the adsorption intensity of adsorbate onto adsorbent. If the value of exponent *n* is greater than 1 then the adsorption represents favorable adsorption conditions [11, 8].

3. Results and discussion

3.1. Characterization of silica gel

XRD, FTIR and SEM characterizations of the silica gel and the kaolin by-products were carried out and cited in our precedent works [12]. Briefly, the chemical composition of kaolin by-product (GOO) was determined by X-ray fluorescence shows that the amount of SiO_2 is up to 92%, this was confirmed by diffraction X analysis. The XRD analysis indicates that the silica gel obtained is amorphous, the surface morphology and pore structure of the representative silica gel prepared at pH 2, which was investigated by SEM presents a great number of pores giving a spongy texture [12].

The observations in SEM image were further confirmed by the pore size and the pore volume of the silica gel (Table 1). The material prepared presents a pore volume of 0.2cm^3/g, with a pore diameter of 17.7Å. These results confirm the mesoporous character of the synthesized silica gels (pore diameter under of 50 Å).

Table1: Surface area, pore volume and average pore radius of silica gel sample prepared from by-product of kaolin [12]

BET surface area (m^2/g)	***BJH desorption values***		
	Surface area (m^2/g)	*Pore volume (cm^3/g)*	*Average pore radius(A°)*
477	*150.4*	*0.2*	*17 .7*

The ATG curve (figure 2) shows a loss of mass in two well-defined regions:

- The first produced at a low temperature, from room temperature to 200 ° C. The mass loss is 12%.
- The second starts from 800 to 900 ° C, we estimate a loss in mass of about 2%.

The ATD curve has an endothermic peak at 70 ° C attributed to the removal of physisorbed water molecules, and another endothermic peak at T= 900°C corresponding to the melting of the NaCl crystals formed during gelation.

Fourier transform infrared spectrometer (FTIR) spectra of Silica gel before and after adsorption of MB dye are given in Figure 3. The spectrum presents wide peak at 3450cm^{-1} attributed to hydrogen bonded silanol (Si-O-H) groups , the band at 1640cm^{-1} may be due to the bending vibration of H_2O molecules. The very strong and broad band at 1075 assigned to Si-O-Si asymmetric stretching vibrations. The weak band at 950cm^{-1} can be assigned to Si-OH and /or $Si-O^-$ groups. This last band has disappeared in the IR spectrum of silica gel after adsorption of MB dye. The shift in the wavenumber corresponds to the variation of the functional groups energy, this indicates the existence of bond process of MB on the surface of silica gel powder.

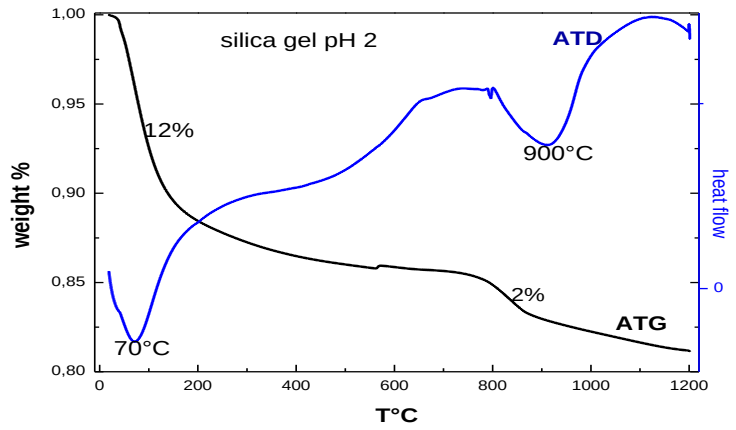


Figure 2. ATG / ATD curves of the silica gel

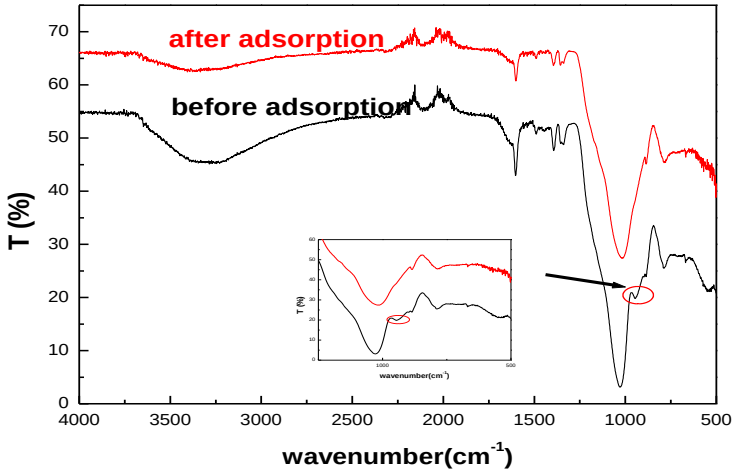


Figure 3: FTIR spectra of silica gel before and after MB adsorption

3.2. Effect of various parameters on the MB Adsorption

The adsorption equilibrium is a process that depends on several parameters such as adsorbent dose, contact time, medium pH, ionic strength, temperature, agitation speed, and concentration. In this study, we have investigated the following parameters: adsorbent dose, contact time, dye concentration temperature and pH of the solutions.

3.2.1. Effect of adsorbent dose

The effect of adsorbent dose on the amount adsorbed of MB dye examined in the range of 0.01-0.15g is illustrated in Figure 4. The results indicate that the uptake of the dye increases with the concentration of the silica gel sample and that the maximum dye removal was achieved for a concentration of 1g/L (0.1g). In fact, the dye removal increased from 10 to 79mg/g when the concentration of the adsorbent was varied from 0.01 to 0.15g/L (0.1 to 1.5g). This can be explained by the presence of a high number of active sites in this mass interval. Beyond this concentration, the yield becomes constant because the addition of silica gel most likely results in partial agglomeration and thus restricts the active surface area available for dye adsorption. The adsorbent dosage was fixed at 0.1g (1g/L) for the remaining experiments.

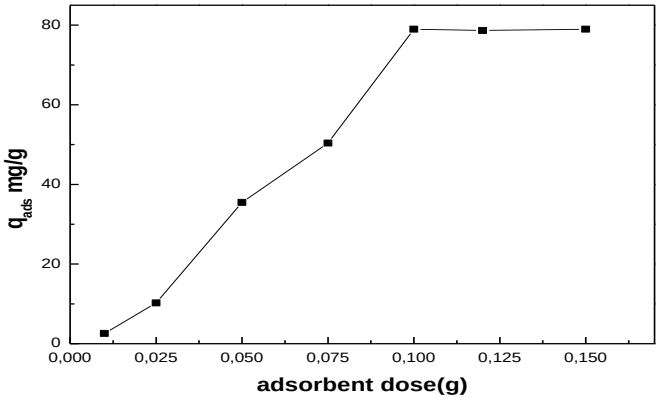


Figure.4 : effect of adsorbent dose on the amount adsorbed of MB dye (C_i=100mg/L , V=100mL, T=25°C, initial pH=6, 3)

3.2.2. Effect of Contact Time

The study of the MB adsorption versus contact time on silica gel prepared at pH 2, obtained from Algerian siliceous by-products of kaolin, is reported in figure 5.

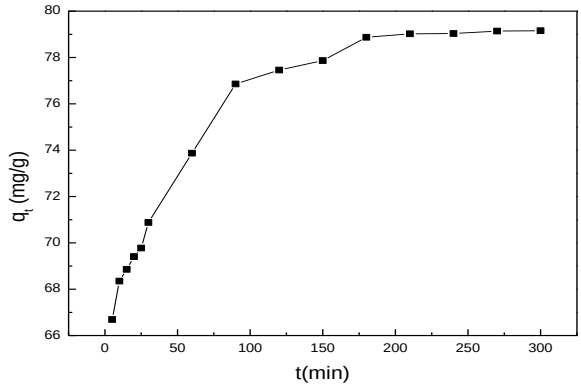


Figure. 5: Effect of time on adsorption of MB dye on silica gel ($m_{adsorbent}$ = 0.1 g, V= 100mL, C_i = 100 mg/L, T = 25 °C, time=300min, initial pH of MB solution=6.3)

The adsorption process was found to be fast at the beginning and then becomes increasingly slow with the approach of saturation. It appears that the adsorption equilibrium is reached at 180 min (q_e =79 mg/g). The fast kinetic of the adsorption process at the beginning of the reaction can be explained by the large number of active sites available, and gradually as the recovery rate of the surface increases, the accessibility of the remaining vacant sites becomes difficult, as a result, the rate of adsorption becomes slow [17].

3.2.3. Effect of pH

The pH is an important factor in the adsorption process, it can influence at the same time the structure of adsorbent and adsorbate as well as the mechanism of adsorption. The effect of pH on the amount of MB removed was studied over the pH range of 2.0 to 10.0. The adsorption and dye concentration were measured after 240 minutes. The results are shown in Figure 6. The silica gel has an accessible hydrophilic surface for the adsorption of the cationic species, so it can be considered that the cationic MB is adsorbed on the edges of silica gel forming bonds with the hydroxyl silanol SiOH forms [18], we

therefore deduce that the availability of the sites intended to fix the cationic dyes is dependent on the pH. In general,

The adsorption capacity increases with increasing pH values (2 to 5). It was observed that the maximum removal of MB was recorded at pH 5. At low pH values, the adsorption capacity is low, this is may be due to the presence of polar groups (Si-OH) on the surface of silica gel (Figure 6) which react with H^+. The lower adsorption of Methylene blue at low pH value (acidic condition) is due to the presence of excess H^+ ions [19], competing with dye cations for the adsorption sites of the adsorbent, which is in agreement with [20, 21].

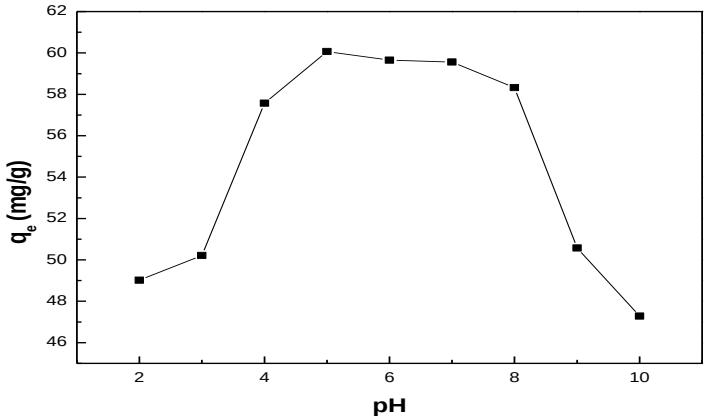


Figure 6: Effect of pH on the adsorption capacity of MB on silica gel (C_i = 50 mg/L, V=100mL, T = 25 °C, Time = 240 min, $m_{adsorbent}$=0.05g).

At higher pH (pH >pH_{pzc}=7.1) the surface of silica gel particles becomes negatively charged. Generally the retention of a cation on an adsorbent increases with increase in the negative charge of the surface. This explains that retention is more remarkable when pH is greater than 5. However, this loss of efficiency when pH increases, shows that the reaction is rather complex and far from being a simple attraction electrostatic between opposite charge species. This decrease in the adsorption capacity at pH > pH_{pzc}=7.1 can be explained by: OH^- ions are attached to cationic dye particles by electrostatic attraction, to forme MBOH hydroxide species which is adsorbed much less. The capacity of an adsorbent to remove dye from the aqueous solution depends on the material surface charge and pH of the solution [22, 23].

3.2.4. Effect of initial concentration

The effect of the initial concentration of MB is shown in Figure 7. The results show that the MB adsorption capacity increases with the increase in the initial concentration of dye, as would be expected. Similar behavior was obtained in the case of adsorption of methylene blue on Cu (II)-exchanged montmorillonite [17], and on cotton fiber [24]. To define the type of adsorption isotherm, we have represented the quantity of equilibrium adsorbed dye as a function of the equilibrium concentration of the solution (Figure 8). The comparaison of the adsorption isotherm of the dye on the silica gel with those established by Giles et al [25] shows that this isotherm is of type IV. This type of isotherm is obtained when only the first layer is in formation.

3.2.5. Adsorption isotherm

The modeling of the experimental results by the Langmuir and freundlich isotherms, exploited in their linear form is represented on the figures 9-a and 9- b.

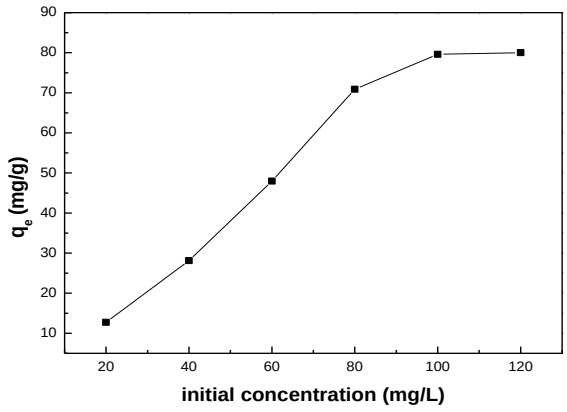


Figure 7: Variation of the amount adsorbed versus initial concentration of dye (T=25°C, t=240min, m=0.1g, V=100Ml, initial pH=6.3)

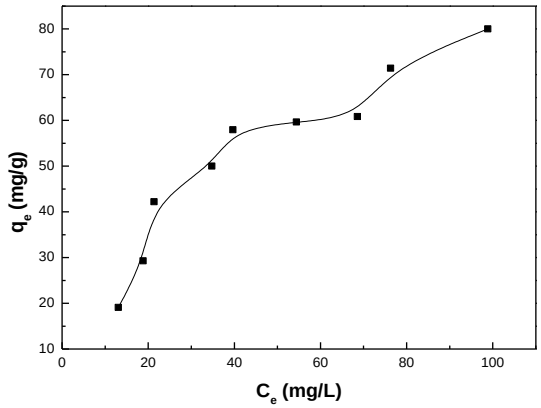


Figure 8: Adsorption isotherms of MB on silica gel at T = 25 °C, time = 240min at the initial pH of MB.

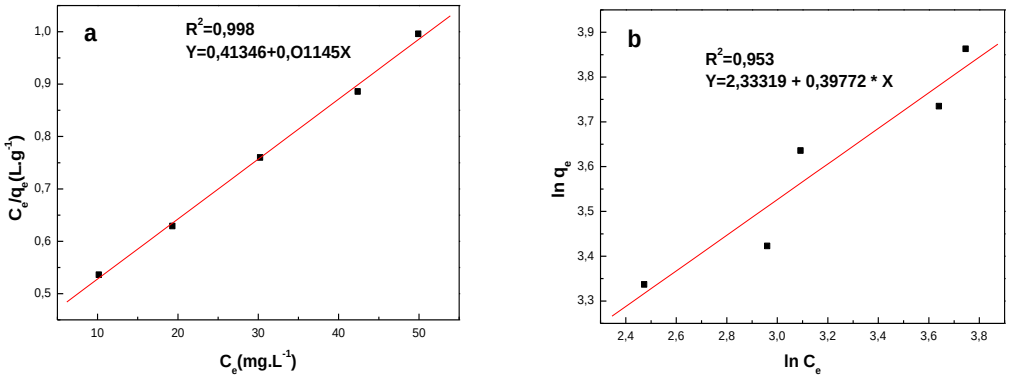


Figure.9: modeling of the experimental results (a) Langmuir, (b) Freundlich

Table2: Langmuir and Freundlich parameters for MB adsorption.

LANGMUIR			FREUNDLICH		
q_{m} (mg/g)	K_L (L/mg)	R^2	K_F(L/g)	n	R^2
87.33	0.027	0.998	10.31	2.5	0.953

From the values in Table 2, the best model for the representation of the results is the Langmuir model, the correlation coefficient is R^2 = 0.998.Langmuir model is valid for monolayer coverage of adsorption of each molecule on a completely homogeneous surface. According to this model, once a dye molecule occupies a site, no further adsorption can take place at the same site.

3.2.6. Effect of Temperature

For better see the evolution of adsorption capacity as a function of temperature, we chose the representation of the adsorption capacity at equilibrium according to the temperature (Figure 10). This curve (figure 10) contains two areas of evolution of the adsorption capacity: In the first part of this curve, for temperatures varying between 25 and 35 °C, a slight increase in the adsorption capacity is noticed when the temperature reaches 35 °C. In the second part between 35 and 65°C, there is an important growth of the adsorption capacity until the temperature reaches 65°C.

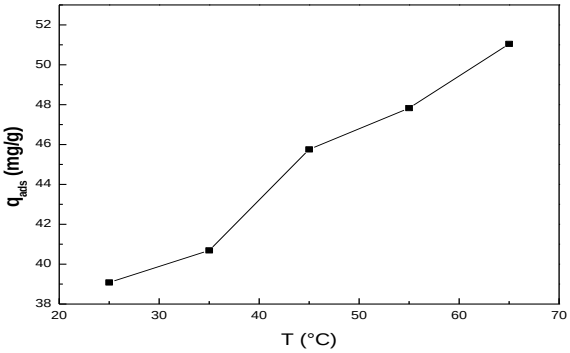


Figure 10: Variation of adsorption capacity of MB on silica gel as a function of temperature. ($m_{adsorpent}$=0.05g, C_i=100 mg/L, V=50mL, t = 240 min. initial pH=6.3)

When the temperature increases, the reaction MB / silica gel becomes easier and we can confirm these results by calculating the thermodynamic parameters related to adsorption process (ΔG, ΔH, and ΔS) according to the equations:

$$logK_d = \frac{\Delta S}{2{,}3\ R} - \frac{\Delta H}{2{,}3RT} \qquad (6)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (7)$$

Where R is ideal gas constant, K_d distribution coefficient for adsorption,ΔS et ΔH entropy and enthalpy of adsorption.

The plot of the experimental results is shown in the Figure 11. The values of ΔH and ΔS are grouped in Table 3 below. The analysis of these thermodynamic parameters shows that the adsorption process is done with spontaneous and favorable reactions (ΔG <0). The positive values of ΔH show that the reactions are endothermic, we note that entropy values are low. The same results were obtained by Yu-Long on a montmorillonite [17] and Ghosh on a kaolinite [18], indicating that the adsorption is done by an endothermic process and with a spontaneous and favorable reaction.

ΔG decreases with increasing temperature of the solution. This can be explained by the fact that the adsorption becomes easier. The negative values of ΔG indicate the feasibility of the adsorption process at room temperature and also the spontaneity of the adsorption reaction [19, 26].

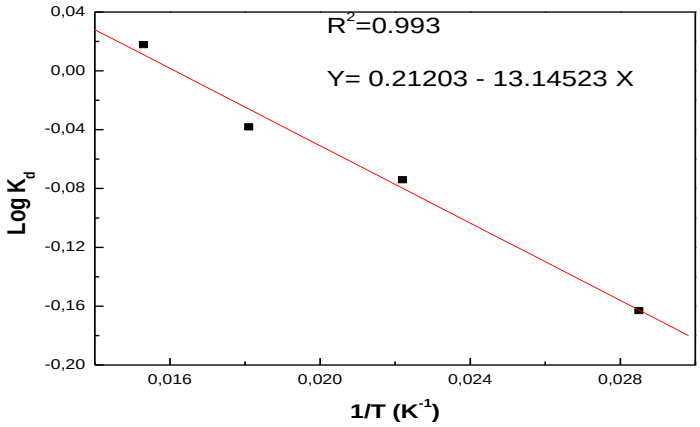


Figure 11: Plot of Log (K_d) versus 1/*T for* estimation of thermodynamics parameters for MB adsorption onto silica gel ($m_{adsorpent}$=0.05g, C_i=100 mg/L, V=50mL, t = 240 min. initial pH=6.3)

Table 3: the values of the thermodynamic parameters of MB adsorption on silica gel

adsorbent	T (°K)	ΔG (kJ.mol^{-1})	ΔH (kJ.mol^{-1})	ΔS (KJ.K^{-1}.mol^{-1})	R^2
Silica gel	298	-957.889	251.693	4.059	0.993
	308	-998.479			
	318	-1039.069			
	328	-1079.659			

3.2.7. Adsorption kinetic studies

The kinetic investigation is performed to determine the efficiency of dye adsorption onto adsorbent. Kinetic studies were fulfilled initial dye concentration of 100mg/L and a temperature of 25°C. Several kinetic models such as the pseudo first- and second order equations and intra-particle diffusion equations have been used to examine the controlling mechanism of the adsorption process**.**

The linear pseudo-first order equation can be defined as [8]:

$$\log(q_e - q_t) = logq_e - \frac{K_1}{2{,}303}t \qquad (8)$$

Where q_t and q_e are the amounts of adsorbed MB at time t and equilibrium (mg. g $^{-1}$), respectively, and k_1 is the rate constant of the pseudo first-order adsorption process (min^{-1}). The slope and intercept of the plot Log (q_e-q_t) versus t (Fig. 11(A)) were used to determine the first-order rate constant (k_1) and the amount adsorbed when the equilibrium (q_e) was reached. The linear pseudo second-order equation is given as follows [8]:

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{t}{q_e} \qquad (9)$$

Where k_2 is the pseudo second-order rate constant (min^{-1}.g .mg^{-1}). The slopes of the plots t/q_t versus t give the value of q_e and the intercept give k_2 (Fig.12 (B))

All the results are summarized in Table 4. In addition to the linear regression, standard statistics of root mean squared error (RMSE=χ^2) and average relative error Δq (%) were also carried out to support the best fit adsorption kinetic model. RMSE is a standard way to measure the error of a model in predicting quantitative data. Can be expressed as:

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(q_{\exp} - q_{cal}\right)^2}{q_{cal}} \qquad (10)$$

Δq (%) Average relative error expressed as :

$$\Delta q(\%) = 100\left(\frac{\sum_1^n \frac{(q_{exp}-q_{cal})^2}{q_{cal}}}{n-1}\right) \qquad (11)$$

Where, q_{exp} and q_{cal} (mg/g) dye uptake values observed experimentally and calculated using kenetic model, respectively.

From the obtained results (table 4), it is deduced that the MB adsorption on the silica gel is better described by the pseudo-second-order equation. The correlation coefficient (R^2) for the second-order kinetics equation is near 1.0. Calculated q_e values showed good agreement with the experimental data

and we can confirm these results by calculating χ^2 and Δq. The pseudo first order was unable to fit experimental data with low R^2 and high χ^2 value. These results suggest a chemisorption mechanism, involving covalent forces through sharing or exchange of electrons between sorbent and sorbate [27]. Similar trends have been reported by Ghorai et al [28], where the pseudo-second order kinetics generated the best fit in comparison to pseudo-first order. Fuat et al**.** [29] and Shasha et al [30] reported the same trend for adsorption of MB and CR respectively.

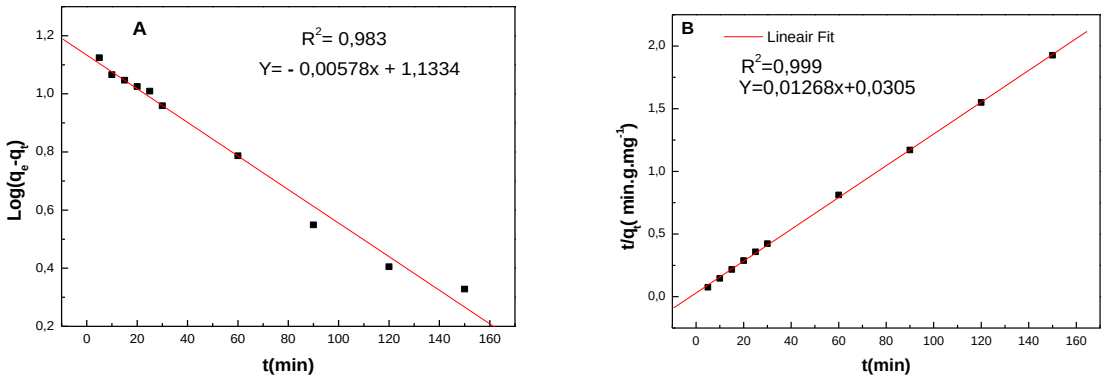


Figure 12: Kinetics by the pseudo-first-order (**A**) and pseudo-second-order (**B**) models for MB dye adsorption on silica gel**.**

Table.4. Pseudo-first and second order parameters for MB dyeadsorption

pseudo-first-order					$q_{e(exp)}$ mg/g	pseudo-second-order				
k_1 (min^{-1})	q_e (mg/g)	R^2	χ^2	Δq (%)		k_2 (g/mg.min)	q_e (mg/g)	R^2	χ^2	Δq (%)
0.0133	13.60	0.983	995	/	79	0.0052	78.86	0.999	1.79	19.88

Comparison of adsorption capacity with different adsorbent reported in literature.

Comparison of maximum adsorption capacities (based on the Langmuir adsorption isotherme) of using various adsorbents were reported in table 5. The results obtained experimentally in this study are very high compared to other investigations. This clearly indicates that the silica gel from Algerian siliceous by-products of kaolin can be used as an adsorbent for cationic dye removal.

Table 5: Comparison of the maximum adsorption capacity of MB on various adsorbents

Adsorbent	**Adsorption capacity (mg/g)**	**References**
Fly Ash-based Geopolymer	37.04	**[8]**
silica gel from Tunisian sands	83.33	**[5]**
Wood ashes	50	**[11]**
crushed brick	96.61	**[31]**
cedar sawdust	142.36	**[31]**
perlite	8.79	**[32]**
Natural Zeolite	23.6	**[33]**
Co_3O_4/SiO_2 nanocomposite	53.87	**[34]**
Silica gel from siliceous by- broducts of kaolin	80.45	This work

Conclusion

This work was undertaken in order to exploit the by-products of kaolin (sand) for the preparation of silica gel and to study their potential retention of a cationic dye (methylene blue, MB). The obtained gel is amorphous which is promising for gel–glass conversion. Silica gel in the form of powder, obtained at pH 2, could reach a specific surface area up to 477 m^2/g. These characteristics display a very porous texture and, consequently, a great capacity of adsorption for this gel.

The results showed that the adsorption may reach 80% of the total adsorption capacity. The amount of MB adsorbed was found to increase with increasing initial dye concentration, solution pH and temperature. When varying the batch temperature from 25 to 65 °C, the adsorption capacity of silica gel was increased slightly. Experimental results showed that the temperature positively affects the adsorption phenomenon as the high energy input overcomes the repulsive forces localized at the interfaces of the liquid and solid media.

The equilibrium data have been analyzed against Langmuir and Freundlich models. The characteristics parameters for each isotherm have been determined. The results indicated that the adsorption equilibrium data fitted well the Langmuir model with R^2 values higher than 0.99. And this reveals that adsorption process corresponds to monolayer coverage of MB molecules over the surface of the silica gel sample. The pseudo-second order expression (R^2 equals to 0.999) is better fitted to describe the adsorption kinetics.

References

1. J. M. Gómez, J. Galán, A. Rodríguez, G. M. Walker, Dye adsorption onto mesoporous materials: pH influence, kinetics and equilibrium in buffered and saline media. *J. Environ Manage* 146 (2014) 355-61. https://doi.org/10.1016/j.jenvman.2014.07.041
2. J. Lin, H. Zhang, H. Hong, H. Liu, X.A. Zhang, Thermally Conductive Composite with a Silica Gel Matrix and Carbon-Encapsulated Copper Nanoparticles as Filler. *Journal of Electronic Materials* 43 (2014) 2759-2769. https://doi.org/10.1007/s11664-014-3159-5
3. Y. Liu, J. Shen, B. Zhou, G. Wu, Z. Zhang, Effect of hydrophobicity on the stability of sol–gel silica coatings in vacuum and their laser damage threshold. *Journal of Sol-gel Science and Technology* 68 (2013) 81-87. https://doi.org/10.1007/s10971-013-3137-z
4. Q. Xu, P. Yin, G. Zhao, Synthesis and characterization of silica gel microspheres encapsulated by salicyclic acid functionalized polystyrene and its adsorption of transition metal ions from aqueous solutions. *Central European Journal of Chemistry* 8 (2010) 214-222
5. K. Lazaar, W .Hajjaji,R.C. Pullar, J.A.Labrincha, F. Rocha,F. Jamoussi, Production of silica gel from Tunisian sands and its adsorptive properties, *Journal of African Earth Sciences* 130 (2017) 238-251
6. A. Adak, M. Bandyopadhyay, A. Pal, A. 2005. Adsorption of anionic surfactant on alumina and reuse of the surfactant-modified alumina for the removal of crystal violet from aquatic environment. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 40 (2005) 167-182
7. F. N. Allouche, N. Yassaa, H. Lounici, sorption of Methyl orange from aqueous solutions on chitosan biomass, Proced Earth and planetary Science 15 (2015) 596-601
8. M. EL Alouani, S. Alehyen, M. EL Achouri, M. Taibi, Removal of CationicDye – Methylene Blue- from Aqueous Solution by Adsorption on Fly Ash-based Geopolymer, *J. Mater. Environ. Sci.* 9 (2018) 32-46
9. A. B. Karim, B. Mounir, M. Hachkar, M. Bakasse, A. Yaacoubi, Removal of basic dye "Methylene Blue" in aqueous solution by Safi clay. *Journal of Water Science* 23 (2010) 375-388.

10. A. Boukraa, F. Messemmeche, Etude qualitative et quantitative de l'adsorption de bleu de méthylène sur le charbon actif en poudre. *Revue Science des Matériaux*, (2016) 25-41
11. N. Fayoud, S. Alami Younssi, S. Tahiri, A. Albizane, Etude cinétique et thermodynamique de l'adsorption de bleu de méthylène sur les cendres de bois (Kinetic and thermodynamic study of the adsorption of methylene blue on wood ashes), *J. Mater. Environ. Sci.* 6 (2015) 3295-3306
12. D. Brahmi, D. Merabet, H. Belkacemi, T.A. Mostefaoui, N. Ait Ouakli, Preparation of amorphous silica gel from Algerian siliceous by-product of kaolin and its physico chemical properties, *Ceramics International* 40 (2014) 10499– 10503.
13 : S.W. Hwang, H.H. Jung, S.H. Hyun, Y.S. Ahn, Effective preparation of crack free silica aerogels via ambient drying, *J. Sol Gel Sci. Technol.* 41 (2007) 139–146
14. Z. Graba, S. Hamoudi, D. Bekka, Na. Bezzi, R. Boukherroub, Influence of adsorption parameters of basic red dye 46 by the rough and treated Algerian natural phosphates, *Journal of Industrial and Engineering Chemistry* 25 (2015) 229–238
15. I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40(9) (1918) 1361-1409, https://doi:1361-1403.10.1021/ja02242a004
16. H. M. F. Freundlich, "Over the Adsorption in Solution," *The Journal of Physical Chemistry*, 57 (1906) 385-471.
17. Y. L. Ma, ZI. R. Xu , T. Guo, P. You, Adsorption of metylene bleu on Cu (II)-exchanged montmorillonite. *Journal of Colloid and Interface Science,* 280 (2004) 283–28
18. D. Ghosh, K.G. Bhattacharyya, Adsorption of metylene bleu on kaolinite. *Applied Clay Science*, 20(2002) 295-300
19. T. J. Nwabanne, O. E. Chenonye, I. K. Philomena, A. C. Christian, O. C. Elijah, isotherm and kinetic modeling of adsorption of dyestuffs onto kola nut (cola acuminata) shell activated carbon, *Journal of Chemical Technology and Metallurgy*, 51 (2016), 188-201
20. R. Rajeshkannan, M. Rajasimman, N. Rajamohan, Decolourisation of malachite green using tamarind seed: Optimisation, isotherm and kinetic studies, *Chemical Industry and Chemical Engineering Quarterly*, 17, 1 (2011) 67-79.
21 : R. Venckatesh, T. Amudha, S. Rajeshwari, M. Chandramohan, M. Jambulingam, Kinetics and equilibrium studies of adsorption of direct red-28 onto Punica granatum carbon, *Int. J. Eng. Technol.* 2, 6 (2010) 2040-2050.
22. E. A. N. Simonetti, L. Cividanes, T. Moreira, B. Rossi, Carbon and TiO_2 synergistic effect on methylene blue adsorption, *Materials Chemistry and Physics* (2016) 1-9.
23. N. Fayoud , S. Alami Younssi , S. Tahiri , A. Albizane, Etude cinétique et thermodynamique de l'adsorption de bleu de méthylène sur les cendres de bois (Kinetic and thermodynamic study of the adsorption of methylene blue on wood ashes), *J. Mater. Environ. Sci.* 6 (11) (2015) 3295-3306.
24. C. Kaewprasit, E. Hequet , N. Abidi, J.P. Gourlot, Application of Methylene Blue Adsorption to Cotton Fiber Specific Surface Area Measurement: Part I. Methodology. *The Journal of Cotton Science*, 2 (1998) 164-173.
25. CH. Giles, D. Smith, A. Huitson (1974a). A general treatment and classification of the solute adsorption isotherm. I: theoretical. *Journal Colloid Interface Science* 47:755–765
26. S. Goswami, U.C. Ghosh, Studies on adsorption behavior of Cr (VI) onto synthetic hydrous stanniz oxide, *Water S.A.*, 31,4 (2005) 597-602
27. B. Abbad, A. Lounis, K. Taibi and M. Azzaz, Removal of Methylene Blue from Coloured Effluents by Adsorption onto ZnAPSO-34 Nanoporous Material, *J. Material Sci. Eng.* 2013, 2:3

28. S. Ghorai,A.K. Sarkar, A.B. Panda,S. Pal, Effective removal of Congo Red dye from aqueous solution using modified xanthan gum/silica hybrid nanocomposite as dsorbent. *Bioresource Technology*. 144 (2013) 485-491.
29. G. Fuat, A. Onder, A. Gulbahar, Application of pomegranate (Punica granatum) pulp as a new bioserbent for the removal of a model basic dye (methylene blue), *Appl. Scie. J.* 20(7) 2012 965-975.
30. D. Shasha, M. Mupa, N. Muzarabani, L. Gwatidzo, C. Machingauta, Removal of Congo red from aqueous synthetic solutions using silica gel immobilized Chlorophyta hydrodictyyon Africanum, *Journal of Environmental Science and Technology*. 8 (2015)83-90.
31. O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, *Journal of Hazardous Materials B,* 135 (2006) 264-273. https://doi.org/10.1016/j.jhazmat.2005.11.062
32. M. Dogan, M. Alkan, A. Türkyilmaz, Y. Özdemir, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite, *Journal of Hazardous Materials.* 109 (2004) 141-148. https://doi.org/10.1016/j.jhazmat.2004.03.003
33. F. Jafari-zare, A. Habibi-yangjeh, Competitive Adsorption of Methylene Blue and Rhodamine B on Natural Zeolite: Thermodynamic and Kinetic Studies, *Chinese Journal of Chemistry,* 28 (2010) 349–356.
34. H.H. Abdel Ghafar, G.A.M. Ali, O.A. Fouad, S.A. Makhlouf, Enhancement of adsorption efficiency of methylene blue on Co_3O_4/SiO_2 nanocomposite, *Desalination and Water Treatment.* 53 (2013) 2980–2989.