



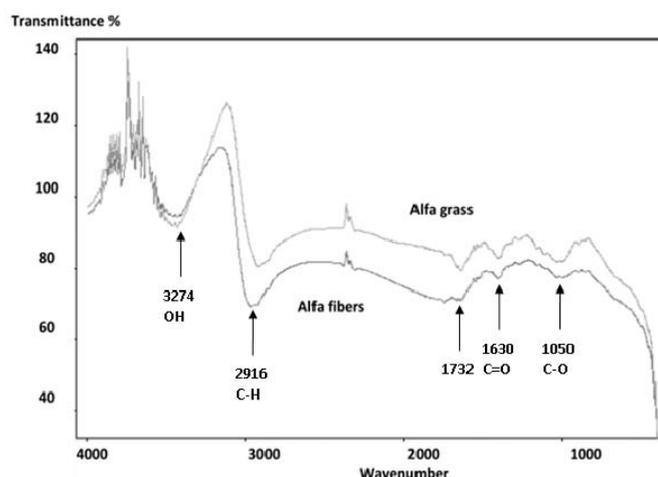
ADSORPTION OF METHYLENE BLUE DYE BY *STIPA TENACISSIMA L* (ALFA FIBERS) IN AQUEOUS SOLUTION: EQUILIBRIUM, THERMODYNAMICS, KINETIC MECHANISM

Sabrina HEMSAS* and Messaoud HACHEMI

Process and Environment Materials Research Unit, M'Hamed Bougara University, Boumerdes, Algeria

Received September 17, 2018

As natural and low-cost material, *Stipa tenacissima L.* fibers were used as an adsorbent to remove methylene blue from aqueous solutions. Alkaline procedure was used to remove non-cellulosic substances to improve sorptive capacity by changing fiber morphology which was analyzed by FTIR, X-ray diffraction, ATG and SEM. A mesoporous structure was developed and the specific surface (S_{BET}) was notably increased from ~ 3 to $62.48 \text{ m}^2/\text{g}$. Batch sorption show that equilibrium was obtained with: 5 g/L of fibers after 40 min at 30°C , the adsorbed dye amount increases with increasing pH. The removal rate was about 99.11%. Experimental data were well described by Freundlich isotherm model; while adsorption kinetic constants fitted with the pseudo-second order one. The adsorption thermodynamics and isotherms found to be consistent with a spontaneous exothermic physic-sorption reaction (negative value of $\Delta H^\circ < 20\text{K Joule/mole}$). Alfa fibers could be used advantageously to eliminate methylene blue from aqueous solutions.



INTRODUCTION

Textile industry wastes represent enormous harm for human health, especially dyes that are used in excess, as a result wastewater is highly concentrated in dye molecules which make biodegradability hard. Decolorization of wastewater took into consideration conventional methods that have been extensively investigated such the use of activated carbon adsorption that was proved efficient,¹ however it remain very expensive. Recently, the usage of agricultural wastes or industrial by-products as low-cost alternative adsorbent is receiving a considerable attention.

The aim of the present research is to develop inexpensive and effective adsorbent from *Stipa tenacissima L.* fibers for the removal of methylene blue dye from aqueous mediums in order to replace existing commercial materials.

Methylene blue (MB) is a cationic dye with broad application such as colorant for paper, hair, cotton and components for drug synthesis. It has been proved to cause retching, stun, cyanosis, jaundice and tissues necrosis in human.² Consequently, there is a need for its removal from wastewater or industrial effluents for more safeguarded environment. Various natural low-cost adsorbents materials such as natural kaolinite,³

* Corresponding author: hemsas_sab@yahoo.fr

clay,⁴ pistachio hull,⁵ oil shale ash,⁶ corn stalks and egussi peeling,⁷ raw and modified rice husk,⁸ potato (*Solanum tuberosum*) plant waste,⁹ and cotton,¹⁰ have been tested for MB removal from wastewater systems, but no studies were conducted about Alfa capacity to capture it. Knowing that Alfa grass or esparto grass (*Stipa tenacissima L.*), this perennial tussock grass, is widely distributed in semi-arid ecosystems of the southern and western Mediterranean basin and mainly in the Maghreb.¹¹

In this study, Alfa cellulose fibers were extracted from *S. tenacissima L.* grass fibers using alkaline procedure to be tested as adsorbent for MB dye. The influence of experimental parameters such as pH, initial dye concentration and temperature of the adsorption process has been investigated. Adsorption isotherm and corresponding kinetic curves were obtained, several adsorption models were used to verify experimental data and to determine adsorption mechanisms. Thermodynamics studies were also carried out to estimate free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes.

MATERIALS AND METHODS

Materials

The *S. tenacissima L.* plants were collected from semi-arid zone (Boussaada, 300 km southern of Algiers). Methylene blue dye (MB) was provided from Merk Co (Germany), its general chemical formula is $C_{16}H_{18}N_3SCl$ with a molecular weight of 373.90 g/mol. It is a green powder that absorbs light at 664 nm.

Extraction of cellulose fibers from *S. tenacissima L.*

Alfa stems of 50-80 cm length were manually cut into approximately 2-3 cm pieces. Cellulosic fibers were extracted using chemical process following El Ghali *et al.*¹² method. First peroxide bleaching was conducted in around-bottomed flask, where was placed 5 g of fresh Alfa, 200 mL of distilled water and 10 mL of H_2O_2 (30%(w/w)). The mixture is stirred for more than 6h at 90 °C. Bleached Alfa was then washed with hot, and cold water therefore dried at room temperature. Cellulose was extracted from Alfa with 400 ml toluene/ethanol mixture (2/1, V/V) for 6h using Soxhlet apparatus.¹³ The second step involved the extraction of cellulosic Alfa fibers using alkaline

procedure. For the alkaline boiling process, the temperature of extraction and the concentration of NaOH solution were fixed, respectively, at 50°C and 0.25M for 4h. The fibers were extracted using liquid to plant ratio of 10:1. At each step of the treatments, the insoluble residue was extensively washed with distilled water. Obtained fibers were dried at room temperature until constant weight. The extraction efficiency (R %) represents the variation of sample weight before and after extraction, it was calculated as Yield of extraction as shown by Equation (1) :

$$R(\%) = 100 * \frac{m_f}{m_a} \quad (1)$$

where m_a and m_f are the weight of dried Alfa before and after extraction, respectively. The value of R was 58% which can be considered acceptable compared with other studied extraction methods.¹⁴

Characterization of alfa fibers

Determination of pH_{PZC}

The zero point of charge (pH_{PZC}) of Alfa fibers was determinate according to the method cited by Belaid and Kacha.¹⁵ 50 mL of 0.01 M NaCl solution was prepared in distilled water. Solutions with different pH ranging from 2-12 were prepared using HCl (0.1 M) or NaOH (0.1 M). Then, 0.15 g of fibers was added to each medium solution and the final pH was measured after 48h under agitation at room temperature. The pH_{PZC} is the point where the curve of final pH vs initial pH crosses the line fitted by final pH vs initial pH.

Plant analysis

Alfa fibers were characterized by elemental analyses, IR spectroscopy, thermal analysis, scanning electron microscopy (SEM). FT-IR spectra were recorded on 4100 JASCO FT-IR spectrophotometer in the range of 4000-400 cm^{-1} for qualitative identification of grass plant and extracted fibers constituents.

Thermal analysis was carried with NETZSCH STA409 thermal analyzer. Both thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the samples were performed up to the temperature of 873K, starting from room temperature in azote atmosphere, with a flow rate of 10 mL/min. Alfa grass was also subjected to XRD analysis with XPERT PRO diffractometer and the SEM micrographs of extracted Alfa fibers were taken using ESEM Philips XL30.

The adsorption-desorption isotherms of the treated Alfa samples were carried out in a BET apparatus on Nova Station A – QuantaChrome instrument. The adsorption gas is nitrogen, and measurements are made at 77.3 K, the sample weight is equal to 88.7 mg and the sample volume equal to 0.12677 cc. The degassing time was of 14 h at 200°C and analysis time was about 144.8 min.

Batch adsorption experiments

Adsorption measurements on Alfa fibers were carried out in batch process to evaluate the effects of various parameters, such as initial dye concentration, contact time, pH and temperature. In each adsorption experiment, 0.5 g of Alfa fibers is added to 100 mL of MB dye solution. The desired pH was achieved by adjustment with HCl (0.1 M) or NaOH (0.1M). Experiments were conducted using jar test (P SELECTA), where mixture is stirred for 2 h at 150 rpm, the aliquots are collected and filtered at pre-determined time intervals, the absorbance of the limpid solutions is measured by an UV- Vis spectrometer (PG instruments CT60) at 664 nm. The adsorbed dye quantity at equilibriums (q_e) and the removal efficiency of Alfa fibers were determined by Equations (2) and (3) respectively:

$$q_e = \frac{(C_0 - C_e) \nu}{m} \quad (2)$$

$$R\% = \frac{(C_0 - C_t) \nu}{C_0} \quad (3)$$

where; q_e (mg/g) and $R\%$ are the adsorption capacity and removal efficiency, respectively. C_0 (mg/L) is initial dye concentration, C_e (mg/L) is dye concentration at equilibrium, m (g) is the sorbent mass and V (L) is dye solution volume.

The temperature influence was conducted by immersing solution in a thermostatic bath, regulated at work temperatures (20, 30, 40 and 50°C) and stirred at 150 rpm.

Kinetic and isotherm studies

The adsorption kinetic is determined by analyzing the quantity of adsorbed dye from aqueous solution at different time intervals. To investigate the effect, the initial dye concentration on the adsorption kinetic different test solutions were prepared with dye concentration between 20 and 50 mg/L. Adsorption Isotherms at various sorbent dosages (2-20 g/L) are analyzed to determine the equilibrium adsorption capacity. Thermodynamics parameters were calcu-

lated from equilibrium adsorption data at different temperatures.

RESULTS AND DISCUSSION

Characterization of extracted fibers

FT-IR spectra

FT-IR spectroscopy studies were carried out to observe the chemical occurring on the Alfa plant induced by chemical modification. Figure 1 shows FTIR spectrum of Alfa grass and fibers. A broad absorption band at 3274-3500 cm^{-1} is mainly due to OH groups, which is lower in intensity after treatment. The band at 2916 cm^{-1} corresponds to CH band present in all natural fibers; the intensity of this peak has decreased during the elimination of hemicelluloses. It is also noted that the 1731.9 cm^{-1} band which corresponds to the non-cellulosic constituents (pectin, lignin, and hemicelluloses) has disappeared as a result of the treatment like found by Benyahia et al.,¹⁶ also a band at 1630 cm^{-1} was found indicating the existence of a C = O band of lignin acetyl groups which is partially reduced on fibers surface. Finally C-O band is observed at 1050 cm^{-1} , it decrease after treatment.¹³

Thermal analyses

TG/DSC curve of Alfa fiber (Fig. 2a) shows that Alfa fibers have an endothermic reaction beginning at about 300°C and ending at 400°C with a maximum at 350.9°C, caused by the evolution of water entrapped by OH- groups present in cellulosic chains,¹³ cellulose decomposition takes place at temperatures higher than 200°C.

X-ray analysis

X-ray diffractogram patterns of fibres are shown in Figure 2b. The major crystalline peak, which was sharp and intense at 22.4°, corresponding to the (002) crystallographic plane family of cellulose I lattice.¹⁷ It is understandable that the cellulose content increases, whereas the amorphous hemicelluloses content decreases during the chemical process.¹³ This is in agreement with Kondo and Sawarti results in¹⁷ Mechi and Mohamed,^{18a,18b} where the authors explain that the interaction of hydrogen bands involving the primary hydroxyl groups result in the formation of crystalline region and contribute to OH- band around 3440 cm^{-1} as shown in the FT-IR spectrum.

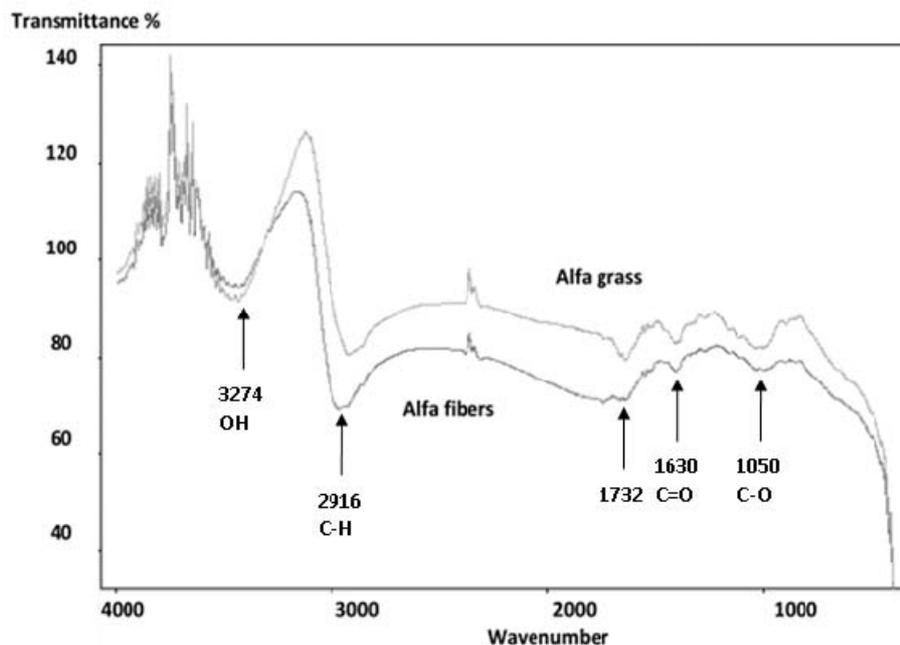


Fig. 1 – FTIR spectrum of Alfa grass and fibers.

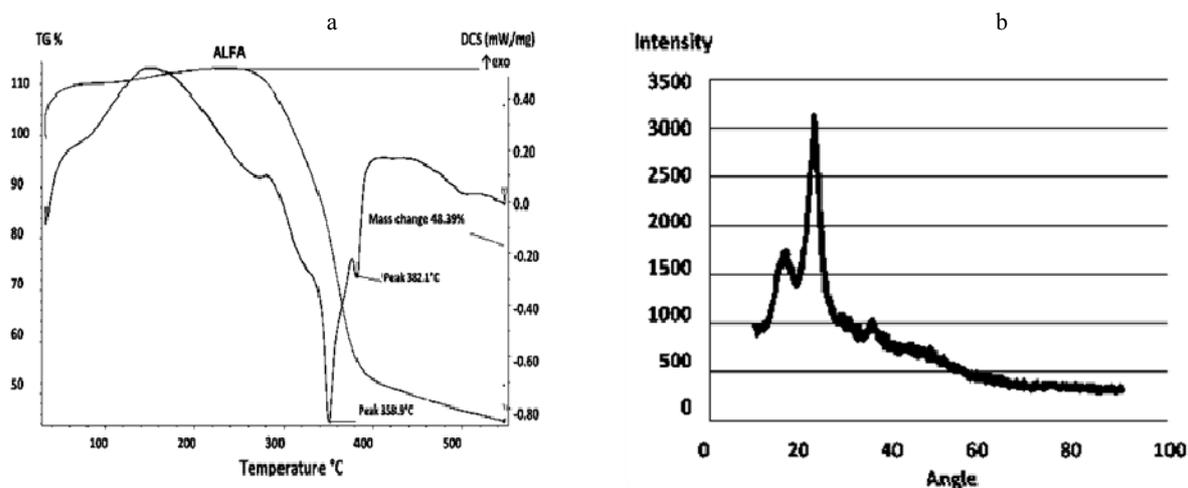


Fig. 2 – Characterization analysis of Alfa fiber a) TG/DSC curve. b) X-ray diffractogram.

Scanning Electron Micrographs (SEM)

Alfa fibers are composed of 48% of cellulosic chains which are the main reinforcement material, leading to microfibrils, which are held together by amorphous hemicelluloses giving fibrils. The fibrils are assembled like numerous layers to build up the structure of the fiber. Fibers or cells are cemented together by lignin, which can be dissolved by alkalinity.¹⁹ The morphology of Alfa fibers was investigated by SEM (Fig. 3); Figure 3a shows that fibers were totally separated by chemical treatment and the adsorbent surface (Figure 3b), presents a heterogeneous aspect with some apparent macro-pores of less than 10 μ m. Those pores were probably naturally present in raw

material, but were partially masked by non-cellulosic coating like cited by many authors,^{16, 19–20} and this fact don't reflect the real sorption potentialities of our material, that's why we needed to explore adsorption-desorption isotherms (BET).

It can be seen above BET (Fig. 4) results that after the alkaline treatment, mesoporous structure was developed (20.88 \AA), increasing the specific surface (62.48 m^2/g) compared to native Alfa plant estimated by Boumehdi Toumi *et al.*²¹ about (3.29 m^2/g). The alkali treatment improved the adsorption features of Alfa while increasing its specific surface and by forming mesopores, what confers an adsorption capacity from afar superior to those met in natural fibers as cotton fiber

(47 mg/g), wool fiber (6.3 mg/g),²² *Posidonia oceanica* L. (5.6 mg/g)²³ and Cotton stalk, wastes and dust with respectively 6,14 and 16 mg/g.²⁴

Adsorption studies

Effect of initial dye concentration and contact time

The effect of initial dye concentration on the sorption is shown in Figure 5.a; the MB sorption amount was quickly increased over the first 20 min then it slow down till 40 min. the equilibrium was acquired within 40 min. the increase in adsorbent loading capacity is in relation with high driving dye ions mass transfer. In fact, the more concentrated the solution, the better the adsorption is.¹⁰

Effect of sorbent dosage

In sorbent dosage experiments, the chosen weights of adsorbent were treated with 100 mL MB

dye solution with constant concentration of 30 mg/L. Figure 5.b shows the effect of Alfa fibers dose on MB dye removal. As the result indicates the removal efficiency increased from 94.52 to 99.11 % with increasing dosage from 2 to 5 g/L and then remained almost constant. This was caused by the fact that with increasing adsorbent dosage more adsorption sites are available.²⁵ However, increasing the sites had little effect on removal efficiency at 5 g/L to 15 g/L because of the establishment of equilibrium at extremely low adsorbate concentration in the solution before reaching saturation adsorption.²⁶ It also can be seen from Figure 4.b that the MB removal efficiency changed slightly from 99.03 % to 99.49 % with an increase in adsorbent dosage from 15 to 20 g/L.

Therefore, 5 g/L of Alfa fibers was chosen as optimum dosage for MB dye removal for next experiments.

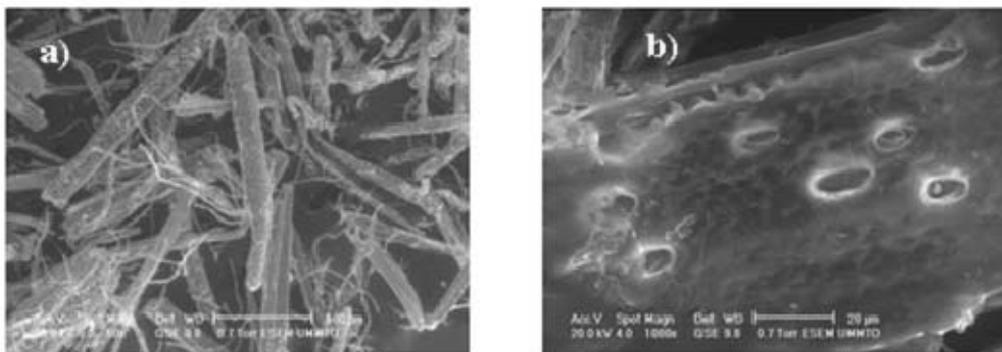


Fig. 3 – Scanning electron micrographs of Alfa fibers.

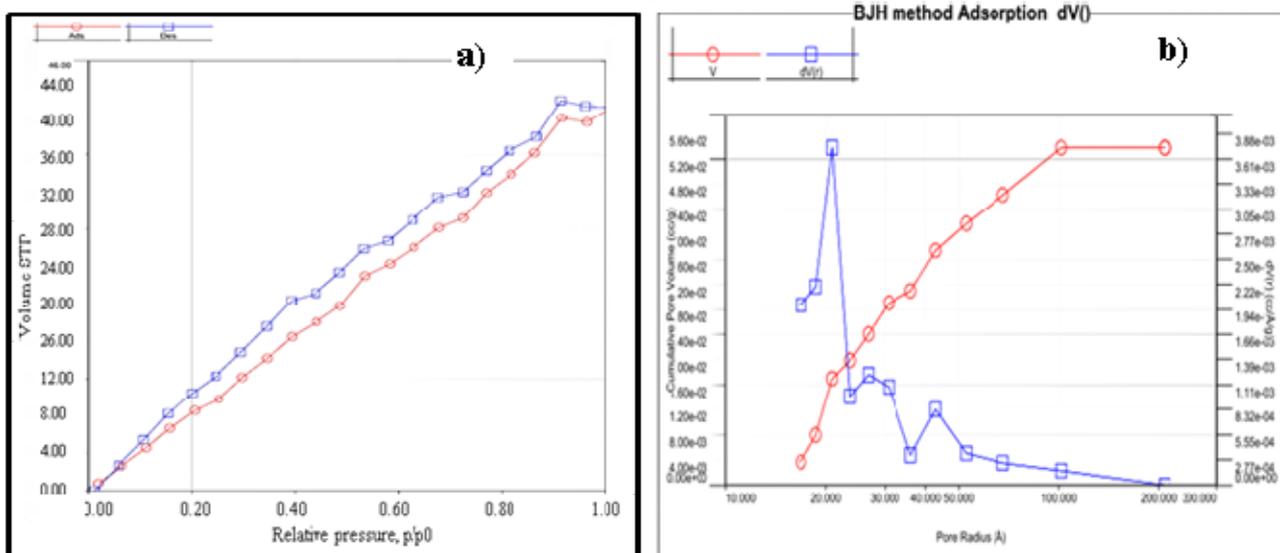


Fig. 4 – a) BET sorption-desorption isotherm b) Pore size distribution of Alfa fibers after alkaline treatment.

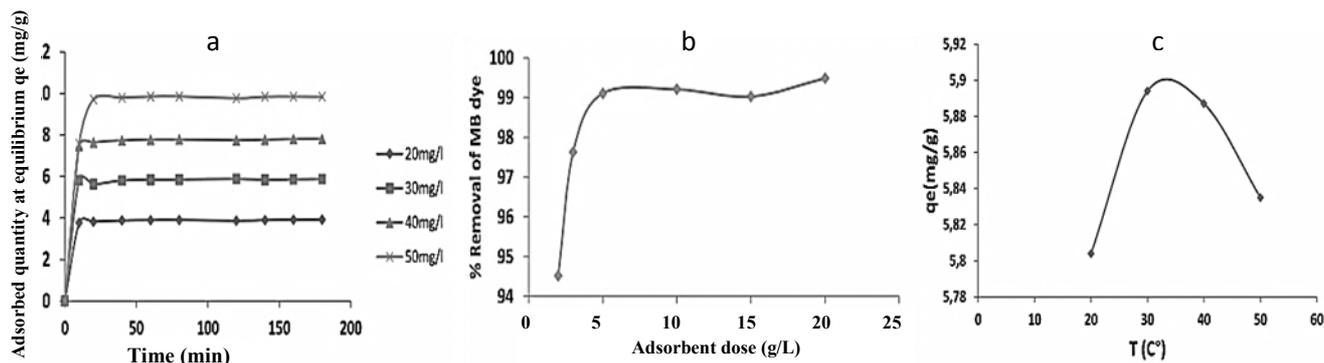


Fig. 5 – a) Effect of contact time on the adsorption of MB dye on Alfa fibers for various initial dye solution concentrations (pH=7, Alfa fibers dose 0.5 g). b) Effect of Alfa fibers dose on MB dye removal for the initial dye concentration ($C_0=30$ mg/L, pH=7 and contact time 120min). c) Effect of temperature on MB dye removal by Alfa fibers ($C_0=30$ mg/L, Alfa fibers dose 0.5 g and contact time 120 min).

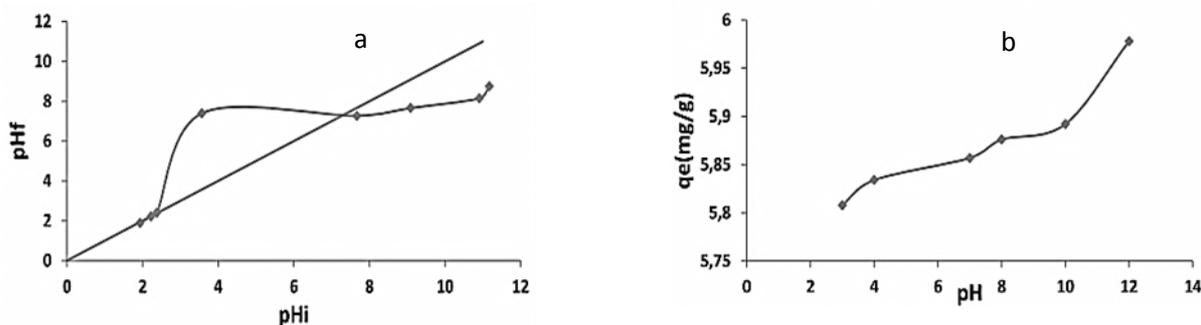


Fig. 6 – a) The zero point of charge (pH_{zpc}) of the used adsorbent for the adsorption experiment. b) Effect of pH on the adsorption of MB dye on Alfa fibers ($C_0=30$ mg/L, Alfa fibers dose 0.5g and contact time 120 min). pH_i: initial pH; pH_f: final pH.

Effect of temperature

Temperature controls two major adsorption aspects; the swelling behavior of the adsorbent and the adsorbate molecules solubility which affects the diffusion rate from the solution to the adsorbent.¹² Figure 5.c shows that the adsorption capacity is very low at 20°C, and above 35°C it decreases with increasing temperature. This is due to the ionic force established between Alfa fibers and MB dye, which is destabilized with temperature increase. This phenomenon may be due to the exothermic effect of the surrounding during adsorption process.²⁷

Effect of pH

One of most important factors controlling the adsorption capacity in aqueous solutions is *pH*. Figure 6(b) shows the influence of *pH* solution on Alfa fibers adsorption of dye; the amount of adsorbed MB dye was found to increase with an increase in pH. This can be explained by the value of the pH_{PZC} (pH_{PZC}=7) of Alfa fibers as shown in Figure 6(a). In fact, as the pH of the system

increased beyond the pH_{PZC} of the adsorbent, the number of negatively charged adsorbent sites increased too, which enhances the adsorption of positively charged MB dye through electrostatic attraction forces.²⁸ Similar pH_{ZPC} values for cotton cellulose was reported by Baghdadi, Mazarji, Sabouhi, Jafari-Kang and Jafari.²⁸

Adsorption isotherms

The adsorption isotherm indicates how the adsorbed molecules are distributed between the liquid and the solid phases at equilibrium. Adsorption isotherms parameters obtained from different models provide important information on the adsorbent surface properties and its affinity with the adsorbate. In this study, Langmuir and Freundlich isotherms were used for the treatments of the equilibrium adsorption data. The Langmuir adsorption isotherm is the best-known linear model for monolayer adsorption and most frequently used to determine the adsorption parameters. Langmuir model is represented by the following Equations (4)-(5):

$$q_e = \frac{K_L \times q_m \times C_e}{1 + K_L \times C_e} \tag{4}$$

$$\frac{1}{q_e} = \left[\frac{1}{K_L \times q_m} \right] \times \frac{1}{C_e} + \frac{1}{q_m} \tag{5}$$

where q_e is the amount of adsorbed dye (mg/g), it represents the adsorptive capacity of the adsorbent for the equilibrium effluent concentration, q_m is the maximum amount adsorbed (mg/g), k_L is a Langmuir's constant signifying energy of sorption (L/mg) and C_e is equilibrium concentration of MB dye in the aqueous phase (mg/L). The Langmuir equations (Equations (4)-(5)) make several assumptions such a monolayer sorption on a surface containing a limited number of sites, predicting a homogenous distribution of sorption energies. The plots of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ are linear and presented in (Fig. 7 b). The values of q_e and K_L have been evaluated from the intercept and slop of these plots (Table 1). The maximum adsorption capacity of monolayer was found to be 83.33 mg/g of Alfa fibers.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter R_L .²⁹ Ho and McKay² established that, the value of R_L indicated the adsorption Langmuir

type to be irreversible ($R=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.217 for concentration of 30 mg/L of MB dye. It means that the adsorption is favorable and the process is reversible.

Moreover, the Freundlich model is an empirical equation that assumes heterogeneous adsorption due to sites diversity. The Freundlich equation is Equation (6):

$$q_e = K_F C_e^{1/n} \tag{6}$$

Equation (6) can be linearized as Equation (7):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{7}$$

where q_e is equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L) of MB dye; K_F and $1/n$ are empirical Freundlich constants which indicate sorption capacity of adsorbent and intensity of adsorption (mg/g), respectively. They are determined from the $\ln q_e$ versus $\ln C_e$ plot (Fig. 7 a). The value of n indicates the degree of non-linearity between solution concentrations and adsorption as follow: if $n=1$, then adsorption is linear, if $n < 1$, the adsorption is a chemical process, if $n > 1$, then the adsorption is a physical process. The n value in Freundlich equation was found to be 1.215 for Alfa fibers, since it is between 1 and 10, the adsorption of MB dye onto Alfa fibers is physical process.

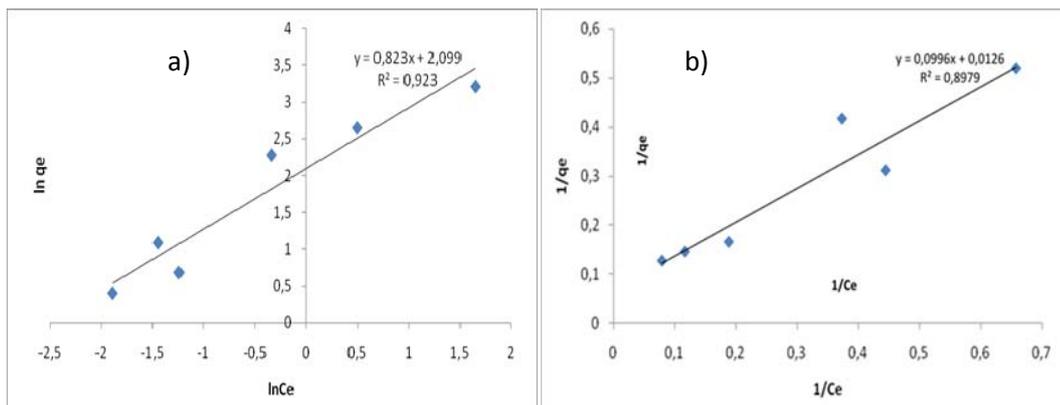


Fig. 7 – a) Freundlich adsorption isotherm of MB. b) Langmuir isotherm of MB on Alfa fibers.

Table 1

Characteristic parameters obtained by the Freundlich and Langmuir equations

Langmuir constant			Freundlich constant		
q_m ($mg \cdot g^{-1}$)	K_L ($L \cdot mg^{-1}$)	R^2	K_F ($mg \cdot g^{-1}$)	N	R^2
83.33	8.25	0.897	8.158	1.215	0.923

Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake including the diffusion process at the solid-solution interface; the mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process.²⁹ In order to understand the controlling mechanism of the adsorption process, the pseudo first order, the pseudo second order and intraparticle diffusion models were applied to examine the experimental data. The pseudo first-order rate expression of Lagergren is given by Equation (8):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

where k_1 (min^{-1}) is the rate constant of the pseudo first order adsorption process which is obtained from the slope of the plot of $\log(q_e - q_t)$ vs time and the intercept gives q_e (equilibrium or Maximum adsorption capacity) (Fig. 8 a)

The pseudo second order kinetics given by Ho's equation as Equation (9):

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where k_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$) is the pseudo second order rate constant; the slopes and intercept of plots of

$\frac{t}{q_t}$ versus time were used to calculate the second order rate constant k_2 and q_e (Fig. 8 b).

The possibility of intra-particle diffusion was explored by using an intra-particle model. The corresponding relation is given by Equation (10):

$$q_t = K_{id} t^{1/2} + C \quad (10)$$

where C is the intercept constant and K_{id} is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$).

Kinetic parameters of the applied models and correlation coefficients are summarized in Table 2. The correlation coefficients (R^2) for the pseudo first order kinetic models are low. Moreover, a large difference in equilibrium adsorption capacity (q_e) obtained from the experimental and calculated values were observed, indicating a poor pseudo-first-order fit to experimental data. R^2 of the second order kinetics model was more suitable; in addition, calculated q_e values were perfectly in agreement with experimental data in this case. This suggests that the adsorption data are well represented by pseudo-second-order kinetics⁹. The analysis of kinetic data by other researchers has also shown that the pseudo-second-order equation can be used to simulate with good agreement the adsorption of MB dye.³⁰ The values of K_{id} constants decrease with increase of initial MB concentration; this behavior can be attributed to the decreasing of competition phenomenon on the surface sorption sites at lower concentration.

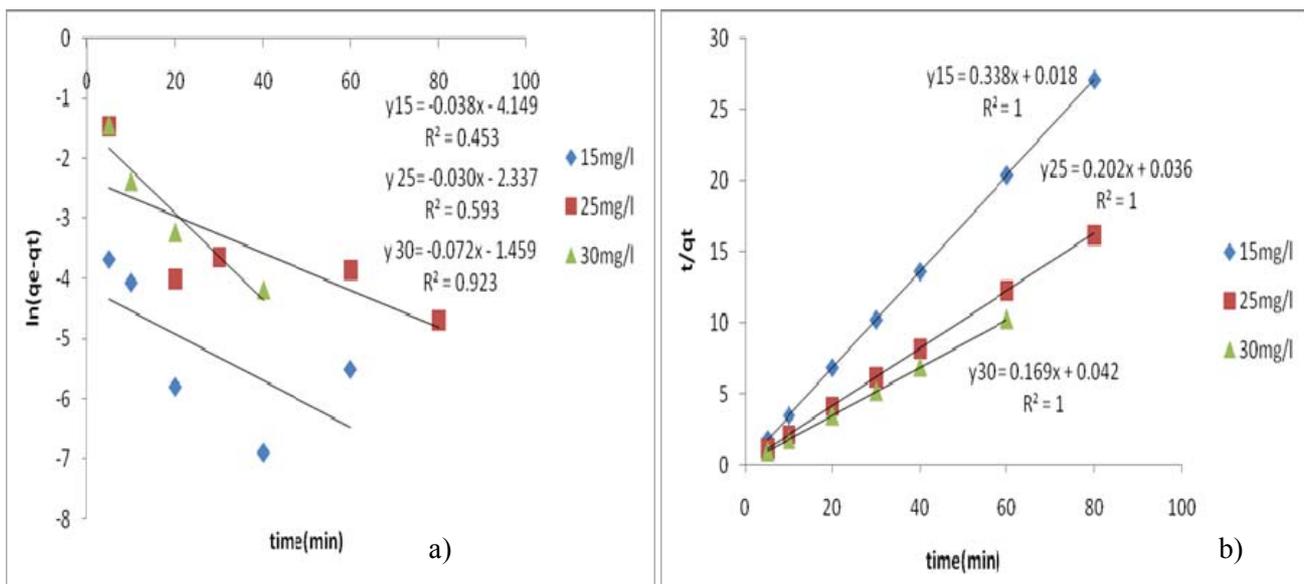


Fig. 8 – a) Pseudo-first-order kinetic for adsorption of MB on Alfa fibers.
b) Pseudo-second-order kinetic for adsorption of MB on Alfa fibers.

Table 2
Kinetic parameters of the adsorption of MB onto Alfa fibers

C ₀ (mg.L ⁻¹)	pseudo-premier ordre				pseudo-second ordre				Diffusion intra particule	
	q _{exp} (mg.g ⁻¹)	k ₁ (min ⁻¹)	q _e (mg.g ⁻¹)	R ²	K ₂ (L.mg ⁻¹ .min ⁻¹)	q _e (mg.g ⁻¹)	R ²	K _{id} (mg.g ⁻¹ .min ^{-0.5})	C	R ²
15	2.95	0.038	0.015	0.45	6.342	2.958	1	0.003	2.928	0.698
25	4.92	0.03	0.096	0.59	1.133	4.95	1	0.02	4.768	0.369
30	5.842	0.072	0.232	0.92	0.68	5.917	1	0.019	5.672	0.364

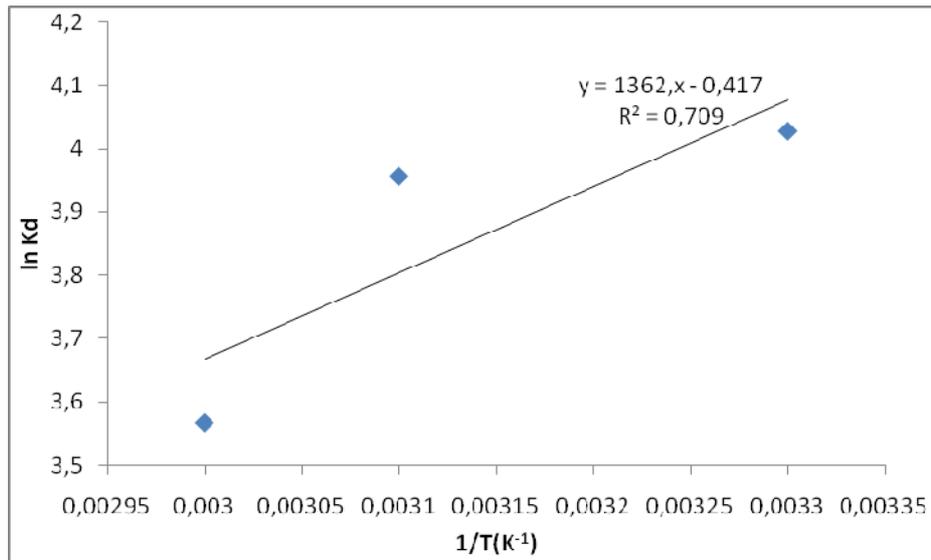


Fig. 9 – Arrhenius plot for adsorption of MB on Alfa fibers (C₀= 30 mg/L, pH = 7, Alfa fibers dose 0.5 g).

Table 1

Thermodynamic parameters for the adsorption of MB dye on Alfa fibers

T (K)	ΔG° (KJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)	ΔH° (KJ.mol ⁻¹)
303	-10.146		
313	-10.294	-3.465	-11.318
323	-9.581		

Thermodynamic parameters

To study the effect of thermodynamic parameters such as the change in Gibb’s free energy (ΔG°), the change in entropy (ΔS°) and the change in enthalpy (ΔH°) were also investigated and calculated for adsorbent using the following Equations (11)-(12)-(13):

$$\Delta G = -RT \ln K_d \tag{11}$$

$$K_d = \frac{C_{Ad}}{C_e} \tag{12}$$

$$\ln k_d = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{R} \right) \frac{1}{T} \tag{13}$$

where k_d is the equilibrium constant, C_{Ad} is the amount of dye adsorbed on solid at equilibrium (mg/L), C_e is the equilibrium concentration of dye in the solution (mg/L), R is the gas constant (8.314 J/ mol.K), and T is the temperature in Kelvin. The values of ΔH° and ΔS° can be obtained from the slope and intercept of Vant’Hoff plot of $\ln k_d$ versus $1/T$.

MB dye Adsorption on Alfa fibers decreased, when the temperature increased from 303 to 323 K. The process is thus exothermic. The plots were used to calculate the values of thermodynamic parameters (Fig. 9 and Table 3). The negative values of Gibbs free energy likewise the decrease in this energy values with the increase of

the temperature shows that the adsorption is more favorable at low temperature and confirm the spontaneous nature of this adsorption, whereby no energy input from outside of system is required.³¹ The low value of this heat (<20 K Joule/mole) confirms that it is a physical adsorption.³² The ΔS° could be used to describe the randomness at the adsorbent-solution interface during the sorption.

CONCLUSION

The experimental study was conducted to investigate the potential of Alfa fibers as adsorbent for the removal of methylene blue dye from aqueous solutions.

The operating parameters such as solutions pH, adsorbent dose, contact time, initial MB dye concentration and temperature were optimized to achieve high adsorption efficiency, with neutral pH conditions and short equilibrium time (40 min). Freundlich isotherm model gives the best fit to the experimental data indicating diversity and heterogeneity in the adsorption sites which describe well natural fibers structure. The kinetic data showed that MB adsorption on Alfa fibers most probably follows a pseudo-second-order behavior and the phenomenon has an exothermic and spontaneous character. For all those reasons Alfa fibers could be used in potential applications as economical and environmentally friendly substrate, as they are effective adsorbents to removal methylene blue dye from aqueous solutions under soft conditions.

Acknowledgements. First author would like to thank Mr DR. M. Hassen V Baouab, Miss L. Haderbache, Mr A. Messaad for their valuable help and Mr A. Saifi for SEM analyses.

REFERENCES

1. a) J. Kyung-Won, C. Brian Hyun, H. Min-Jin, J. Tae-Un and A. Kyu-Hong, *Bioresource Technology*, **2016**, *219*, 185–195; b) D. Pathania, S. Sharma and P. Singh, *Arabian J. Chem.*, **2017**, *10*, Supplement 1, S1445-S1451.
2. Y. S. Ho and G. McKay, *Chem. Eng. J.*, **1998**, *70*, 115-124.
3. S. Zhu, L. Tiantian, Z. Jun, C. Yun, Y. Dongxue and W. Yanxin, *Appl. Clay Sci.*, **2014**, *102*, 33-40.
4. R. Elmoubarki, F. Z. Mahjoubi, H. Tounsadi, J. Moustadraf, M. Abdennouri, A. Zouhri, A. El Albani and N. Barka, *Water Res. Ind.*, **2014**, *9*, 16-29.
5. G. Moussavi, R. Khosravi, *Chem. Eng. Research and Design*, **2011**, *89*, 2182-2189.
6. Y. Miyah, M. Idrissi, A. Lahrichi and F. Zerrouq, *Int. J. Innovative Research in Sci., Eng. and Techn.*, **2014**, *03*, 15600-15613.
7. D.-R. Tchuifon Tchuifon, N.-A. Nche George, H.-J. Tchouanyo Dongmo, C. Ngakou Sadeu, A.-L. Djoumbissie, S.-G. Anagho, T. Kamgaing and J. M. Ketcha, *Int. J. Innovative Research in Sci., Eng. and Techn.*, **2015**, *3*, 8-14.
8. F. Kazembeigi, H.-R.-S. Arezoomand, H. Fraji, F. Mohammadi, R. Khoshneyat, A. Nikonahad and H. Nourmoradi, *The veleger*, **2014**, 1-7.
9. N. Gupta, A. K. Kushwaha and M. C. Chattopadhyaya, *Arabian J. Chem.*, **2016**, *9*, S707-S716.
10. L. F. M. tIsmail, H. B. Sallam, S. A. Abo Farha, A. M. Gamal and G. E. A. Mahmoud, *Spectrochim. Acta Part A: Molec. Biomolec. Spectroscopy*, **2014**, *131*, 657-666.
11. D. Trache, A. Donnot, K. Khimeche, R. Benelmir and N. Brosse, *Carbohydr. Polym.*, **2014**, *104*, 223-30.
12. A. El Ghali, M. H. V. Baouab and M. S. Roudesli, *J. Appl. Polym. Sci.*, **2010**, *116*, 3148-3161.
13. A. Meghchiche, A. Haouam and B. Immirzi, *Chem. & Chem. Techn.*, **2013**, *7*, 339-344.
14. O. Faruk, A. K. Bledzki, H.-P. Fink and M. Sain, *Progress in Polym. Sci.*, **2012**, *37*, 1552-1596.
15. K. D. Belaid and S. Kacha, *Rev. des Sci. de l'eau*, **2011**, *24*, 131.
16. A. Benyahia, A. Merrouche, Z. E. A. Rahmouni, M. Rokbi, W. Serge and Z. Kouadri, *Mechanics & Industry*, **2014**, *15*, 69-73.
17. M. D. L. Chikouche, A. Merrouche, A. Azizi, M. Rokbi and S. Walter, *Journal of Reinforced Plastics and Composites*, **2015**, *34*, 1329-1339.
18. a) L. Mechi and B. A. Mohamed, *Int. J. Greenhouse Gas Control*, **2015**, *37*, 243-248; b) K. Obi Reddy, G. Sivamohan Reddy, C. Uma Maheswari, A. Varada Rajulu and K. Madhusudhana Rao, *J. Forestry Research*, **2010**, *21*, 53-58.
19. A. Bessadok, S. Marais, F. Gouanve, L. Colasse, I. Zimmerlin, S. Roudesli and M. Métayer, *Composites Sci. and Techn.*, **2007**, *67*, 685–697.
20. A. Bessadok, D. Langevin, F. Gouanvé, C. Chappey, S. Roudesli, S. Marais, *Carbohydrate Polymers*, **2009**, *76* (1), 74-85.
21. L. Boumehdi Toumi, L. Hamdi, Z. Salem and K. Allia, *Desalination and Water Treatment*, **2013**, *53*, 806-817.
22. A. Rasheed Khan, H. Tahir, f. Uddin and U. Hameed, *J. Appl. Sci. Environ.*, **2005**, *9*, 29-35.
23. M. C. Ncibi, B. Mahjoub and M. Seffen, *J. Hazard Mater.*, **2007**, *139*, 280-5.
24. B. AcemİOĞLu, M. ErtaŞ, M. H. Alma and M. Usta, *Turkish J. Chem.*, **2014**, *38*, 454-469.
25. B. H. Hameed, *J. Hazard Mater.*, **2009**, *162*, 939-44.
26. Z. Yao, L. Wang and J. Qi, *CLEAN - Soil, Air, Water*, **2009**, *37*, 642-648.
27. a) N. Yeddou and A. Bensmaili, *Chem.Eng. J.*, **2006**, *119*, 121-125; b) M. A. M. Salleh, D. K. Mahmoud, W. A. W. A. Karim and A. Idris, *Desalination*, **2011**, *280*, 1-13; c) M. T. Yagub, T. Sen and H. Ang, *Environ. Earth Sci.*, **2013**, *71*, 1507–1519.
28. M. Baghdadi, M. Mazarji, M. Sabouhi, A. Jafari-Kang and A. Jafari, *J. Adv. Chem.*, **2014**, *9*, 2061-2071.
29. P. Senthil Kumar, R. V. Abhinaya, K. Gayathri Lashmi, V. Arthi, R. Pavithra, V. Sathyaselvabala, S. Dinesh Kirupha and S. Sivanesan, *Colloid J.*, **2011**, *73*, 651-661.
30. a) Y. Bulut, N. Gozubenli and H. Aydin, *J. Hazard Mater.*, **2007**, *144*, 300-306; b) H. Demir, A. Top, D. Balkose and S. Ulku, *J. Hazard Mater.*, **2008**, *153*, 389-394; c) G. Crimi, *Dyes and Pigments*, **2008**, *77*, 415-426.
31. P. Senthil Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi and S. Sivanesan, *Desalination*, **2010**, *261*, 52-60.
32. T. Yang and L. Wang, *BioResources*, **2013**, *8*, 4722-4734.

