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Removal of methylene blue from aqueous solution by adsorption on low-cost adsorbent: Mauritanian *Aeschynomene Aspera*

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Abstract - Résumé

Abstract: A low-cost adsorbent, Mauritanian *Aeschynomene Aspera* (AeAs), was used to remove methylene blue (MB) from water. Ionic exchange capacity, swelling and porosity ratios, and adsorption properties of AeAs were investigated. The experimental results show that the average value of ionic exchange capacity of AeAs was 0.3 meq/g. The average swelling and porosity ratios were 78% and 92%, respectively. The adsorption process was found to follow Langmuir model as the correlation coefficient (R^2) was higher than 0.99 whereas the mechanism of adsorption followed the pseudo second order. Results of Attenuated total reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy support the presence of carboxylic groups embedded on adsorbent. Therefore, the adsorption of MB onto AeAs can be assigned to intermolecular interactions between cationic groups embedded on dye molecules and various groups such as carboxylic groups into AeAs material. The maximum adsorption capacity reached 91 mg/g and the values of Langmuir separation factor (R_L) were in the range 0.04-0.217.

Résumé : Cette étude est destinée à mettre en valeur l'utilisation d'un adsorbant naturel de faible coût, *Aeschynomène aspera* (AeAs), pour l'élimination du bleu de méthylène (BM) de l'eau. Les résultats expérimentaux montrent que la valeur moyenne de la capacité d'échange ionique des AeAs était de 0,3 meq/g, la capacité d'adsorption maximale de BM était 91 mg/L, le taux moyen de gonflement était 78% alors que celui de la porosité était 92 %. En outre, les analyses cinétiques montrent que le processus d'adsorption suit le modèle de Langmuir, avec un coefficient de corrélation (R^2) supérieur à 0,99 et un facteur de séparation compris entre 0.04 - 0.217. Quant au mécanisme d'adsorption, il est gouverné par un modèle de pseudo second ordre. Par ailleurs, les résultats de la spectroscopie infrarouge à transformée de Fourier à réflexion totale atténuée (atr-FTIR) confirment que l'adsorbant contient des groupes carboxyliques susceptibles de développer des interactions intermoléculaires avec les groupes cationiques portés par les molécules du colorant.

1. INTRODUCTION

There is no doubt that with the growth of industrialization and world population the natural water sources are more exposed to contamination with hazardous pollutants, which would contribute in the deterioration of water quality. Heavy metals, dyes, pesticides, phenol compounds, pharmaceuticals, rejected products and pathogenic microorganisms are reported to be the main contaminants found in the natural water which constitute a danger on consumers [1].

Driven by the critical problem of water pollution and its impact on people health, investigations on water treatment continue to attract researchers who are exposed to huge difficulties due to the various sources of hazardous pollutants [2, 3]. To overcome this obstacle, the performances of water treatment must be highly improved. This target is not easy to achieve in many countries due to the need for sophisticated

and expensive equipments. Thus, several researchers orientated their investigations to discover low-cost materials or new techniques, which could allow the removal of hazardous pollutants from water [4, 5].

In fact, the first serious attempts based on the use of biomass materials or low-cost absorbent appeared in the latest decades of the 20th century. These low-cost adsorbents were used to remove some pollutants from wastewater [6 - 10].

Several works were dedicated to the removal of MB from water by various conventional and unconventional methods [11-12]. Afroze et al. [13] proposed novel biomass, *Eucalyptus sheathiana* bark, to remove MB from water. Their experimental results showed that the maximum adsorption capacity of MB dye on *Eucalyptus sheathiana* bark was 204.08 mg/g and the kinetic adsorption followed pseudo-second-order. B.H. Hameed et al. [14] demonstrated that jackfruit peels are suitable adsorbents for MB removal. These low-cost adsorbents offer a maximum adsorption capacity of 285.713 mg/g and an adsorption kinetic in conformity with pseudo-second-order equation. Using gypsum as a low-cost adsorbent, Muhammad et al. [5] found that the maximum adsorption capacity of MB was 36 mg/g and the adsorption kinetics followed the pseudo second order equation. Several other works were published on the removal of MB by various low-cost adsorbents [15 - 19].

To improve the capacity of the low-cost adsorbent, chemical processes were applied to modify the structure of adsorbent. Akköz *et al.* [20] used sulfuric acid to activate hawthorn kernel which is an agricultural waste. This process allowed the increase of maximum MB adsorption capacities from 49.5 mg/g for natural bio adsorbent to 151.5 mg/g for sulfonated bio-adsorbent. Shakoor *et al.* [21] found that the maximum adsorption capacity of MB on *citrus limetta* peel bio adsorbent was 227.3 mg/g. Deng *et al.* [22] activated cotton stalk by sulfuric acid and phosphoric acid. This reaction leads to the enhancement of maximum adsorption capacity of MB from 147 mg/g for natural cotton stalk to 222 and 555 mg/g for phosphorized and sulfonated cotton stalks respectively.

This investigation proposes the use of AeAs as a low-cost adsorbent for water treatment. AeAs is an aquatic flowering plant in the family Fabaceae. Its stems are composed of reddish-brown barks which envelop very soft and light whitish wood. This plant is used in many countries to prepare specific artworks [23, 24] or as an organic nitrogen fertilizer (Green Manure) in rice cultivation [25]. To understand the role of intermolecular interaction between dye molecules and AeAs biomaterial, the ionic exchange capacity, swelling and porosity ratios were determined and the effects of time and initial dye concentration were investigated. Moreover, adsorption and kinetics models were applied to highlight the adsorption properties of this biomaterial.

2. EXPERIMENTAL PROCEDURE

Stems of AeAs plant were collected from Aleg-lake. Their barks were removed to get the wood which was washed thoroughly with distilled water, for 3 days, until having a constant conductivity, and then dried at room temperature for 3 days. Afterwards, the wood was cut into small pieces with controlled dimensions.

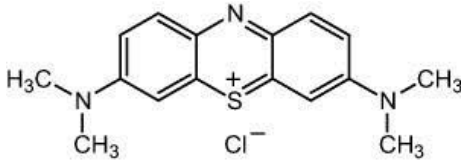
All chemical products were used as supplied, without any further purification. Methylene blue is a cationic compound as shown by Schema 1, its molecular weight is 319.5 g/mol and its maximum absorption was at 650 nm.

2.1. Optical microscopy image

The optical microscopy images of *Aeschynomene* stem were recorded via a Sony TM 3CCD camera adapted to a LeicaTM DMLM microscope, whereas the photo of *Aeshynomene* stem were collected by Sumsung J530F/DS.

2.2. Determination of Ion Exchange Capacity

The ion exchange capacity was determined after alternative sample conditioning in NaOH 0.1 M and HCl 0.1 M for an immersion time of at least 4 hours. In H^+ form, the sample was equilibrated in water for at least 10 minutes to remove the free hydrogen ions. Afterwards the membranes in carboxylic form were immersed for 4 hours, in 50 mL of NaCl 0.01 mol/L. The amount of –COOH groups was determined by titration of 5 mL of immersion solution by NaOH 0.01 M.



Schema 1: Chemical structure of Methylene Blue

2.3. Measurement of Swelling and Porosity ratios

The water content of samples was calculated from the weight difference between the swollen-membrane weight (W_{sw}) and the dried membrane weight (W_{dr}). The swelling ratio (S_r) was determined from the ratio of the water uptake to the swollen-membrane weight [12]:

$$S_r = \frac{W_{sw} - W_{dr}}{W_{sw}}$$

Aeschynomene samples were immersed in Butanol solvent which will empty the pores of samples. The porosity ratio ($P_{r.\,but}$) was determined from the difference between sample weight empty with butanol (W_{but}) and sample weight (W_{free}) free of butanol [26].

$$P_{r.but} = \frac{w_{but} - w_{free}}{w_{but}}$$

2.4. FTIR spectrum recording

Before its mounting on the attenuated total reflection device for FTIR measurements, samples were dried in a vacuum oven at 50°C for 4h. The FTIR spectrometer was a Nicolet AVATAR 360 FT-IR equipped with a Ge ATR crystal. The spectra were recorded at an incident beam angle of 45°. For each sample, the infrared spectrum is the result of 64 scans with a resolution of 4 cm^{-1}.

2. 5. Adsorption of MB on AeAs

Batch adsorption of MB on AeAs was carried out in Erlenmeyer flasks with 25 mL of dye solution at a room temperature of 25°C. The Erlenmeyer flasks containing AeAs samples were agitated at a constant speed of 100 T/min for a known time.

The dye absorption was measured at the wavelength corresponding to the maximum absorption, λ_{max} = 650 nm, using a 6705 UV/VIS spectrophotometer, Model JENWAY.

The amount of dye adsorbed onto the AeAs Q_e (mg/g) was calculated as following [27]:

$$Q_e = (C_0 - C_e) \times V / m$$

Where:

- Q_e is the adsorbed amount of dye (mg/g),
- C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium concentrations of dye, respectively.
- m (g) is the mass of the Aeschynomene sample.
- V (L) is the volume of the liquid phase.

3. RESULTS AND DISCUSSIONS

3.1. Aeschynomene stem images

The Stem of AeAs plant is composed of reddish bark and white wood as shown by visual image represented by Figure 1a. The optic microscopic images, illustrated by Figure 1b, show a different zone's color which might be due to the nature of absorbed compounds

Figure 1a

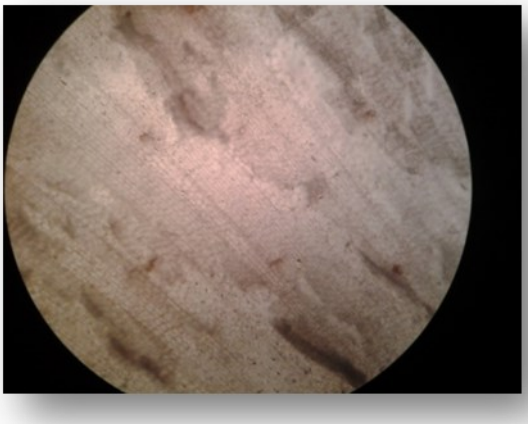


Figure 1b

Figure 1: Samsung phone image of the Section of Aeschynomene stem (1a) and the Optic microscopic section image (1b)

3.2. ATR-FTIR Results

ATR - FTIR is a powerful analytical technique. Then, it is frequently used to study the material structure. Figure 2 illustrates the ATR FTIR spectrum of Aeschynomene Aspira wood.

The ATR FTIR spectrum of Aeschynomene Aspira stem shows several absorption bands at 3200 - 3500 cm^{-1}, around 2900 cm^{-1}, near 1720 cm^{-1} and at 1090 cm^{-1}. The strong band observed between 3200 - 3500cm^{-1} was attributed by many authors to the stretching vibration of O-H groups [28-30,] whereas, the band observed near 1720 cm^{-1} is due to the stretching vibration of C=O groups and the band observed near 1090 cm^{-1} was assigned to the vibration of C-O group. These bands are generally characteristic of cellulose, hemicellulose and lignin structures [28].

3.3. Measurement of ionic exchange capacity, swelling and porosity ratios

Ionic exchange capacity, swelling and porosity parameters are often used to describe material physicochemical properties. The presence of exchangeable sites offers many advantages to material: the removal of opposite charges from treated substance, reduction of fouling effect, increase of material life, etc. Swelling ratio reflected the behavior of hydrophilic materials which undergo an extension, in water medium, due to the water molecules permeability, whereas, the porosity ratio reflected the unoccupied size of material.

Table 1, summarizes the experimental values of ionic exchange capacities (IEC), swelling (**S_r %)** and porosity ratios (**P %)** for three AeAs samples chosen from different parts of wood. The difference between the values of each parameter is due to the heterogeneity of wood composition.

The average value of ionic exchange capacity, 0.3 meq/g, is significant to enhance the exchange between water and AeAs wood. These sites play an important role in dye removal from water [12].

The swelling ratio S_r of different AeAs samples is varying between 70 to 80%, whereas, the porosity ratio reaches 94%. These high swelling and porosity ratio should enhance the water permeability through AeAs structure and might improve the contact between dye molecules and AeAS whole inter surfaces.

3.4. Study of adsorption of MB blue on AeAs

The adsorption capacity Q_t of MB on AeAs was calculated from the experimental results, according to equation 1 and its variation versus time was represented in figure 3.

For both concentrations (100 and 200 mg/L), the adsorption process increases sharply within the first 8 hours and attains progressively equilibrium afterwards. In the first interval, 0 to 8 hours, the rate of adsorption is higher as the adsorbent sites are totally free whereas in the second interval higher than 10 hours, adsorption rate decreases as it approaches to equilibrium (saturation of adsorbent sites). Otherwise, it appears clearly from adsorption curves that equilibrium adsorption increases with the increase of initial concentration. The experimental value of equilibrium adsorption capacity passes from 54 mg/g to 91 mg/g when the initial concentration increases from 100 to 200 mg/L. This behavior might be interpreted as the result of the increase of driving forces of dye molecules from bulk solutions towards AeAs pores [17].

3.4.1. Isotherms' model

At the same conditions of pH, temperature and shaking speed, several AeAs samples with the same masses (0.0615 g) were immersed in MB solutions at different initial concentrations (60, 100, 200, 250, 300 and 400 mg/L). The obtained results were fitted, respectively, according to Langmuir, Freundlich and Temkin isotherms.

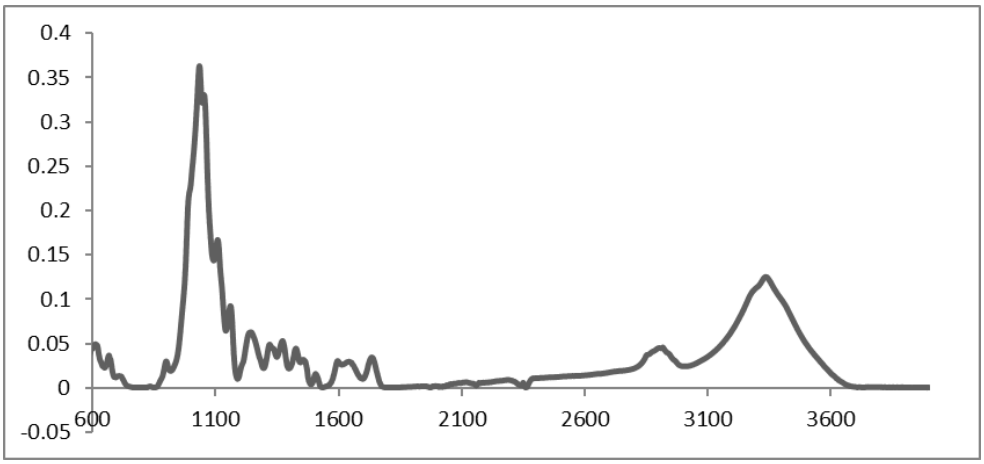


Figure 2. ATR-FTIR spectrum of Aeshynomene Aspira stem

Table 1: Ionic exchange capacity (IEC), swelling (S_r %) and Porosity (P%) ratios for three samples of Aeschynomene aspera taken from different part of wood

Samples	1	2	3
IEC (meq/g)	0.40	0.26	0.20
S_r %	83	80	70
P %	96	95	92

a) Langmuir model

The theoretical model of Langmuir supposes the establishment of intermolecular interactions between adsorbate molecules and adsorbent sites to form a monolayer on the surface of adsorbent. According to this model, the rate of intra molecular interactions between adsorbate molecules is negligible and all adsorbent sites have the same reactivity.

To describe these assumptions, Langmuir proposes the following mathematical equation (model) [31]:

$$\mathbf{Q_e = Q_m K_L C_e /(1 + K_L C_e)}$$

Where:

Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

C_e = the equilibrium concentration of adsorbate (mg/L)

Q_m = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg).

The linearization of this equation leads to the following formula:

$$\mathbf{1/Q_e = 1/Q_m + 1/(K_L Q_m C_e)}$$

The plot of 1/Qe versus 1/Ce, as illustrated by figure 4, indicates a straight line with a correlation coefficient $R^2 = 0.995$ and maximum capacity adsorbent equal to 91 mg/g. Moreover, the determination of Langmuir constant K_L and Langmuir separation factor R_L leads to $K_L = 0.06$ L/mg and R_L values which are lying between 0.04 and 0.217.

The Langmuir separation factor R_L is defined as equal to $1 / (1 + K_L C_0)$ and it is used to evaluate the adsorption process. Adsorption is favorable when the value of R_L is between 0 and 1, linear if $R_L = 0$ and no favorable when the R_L values are greater than 1 [32].

The value of correlation coefficient, $R^2 = 0.995$, proves that the Langmuir model describes perfectly the adsorption of MB on AeAs samples. Furthermore, the values of separation factor which are lying between 0.04 and 0.217 indicate that the adsorption of MB is favorable.

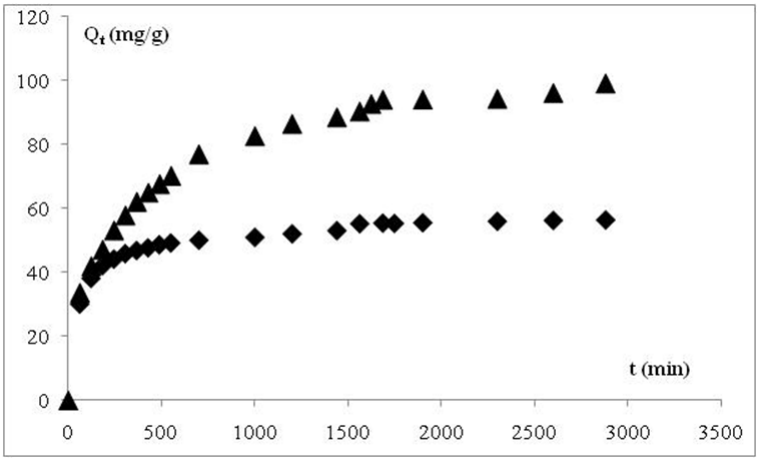


Figure 3: Effect of contact time on adsorption of methylene blue on Aeschynomene aspera at different initial concentrations (▲: 200 mg/L and u : 100 mg/L) and the same pH = 5.5, T=25°C and 100 rpm.

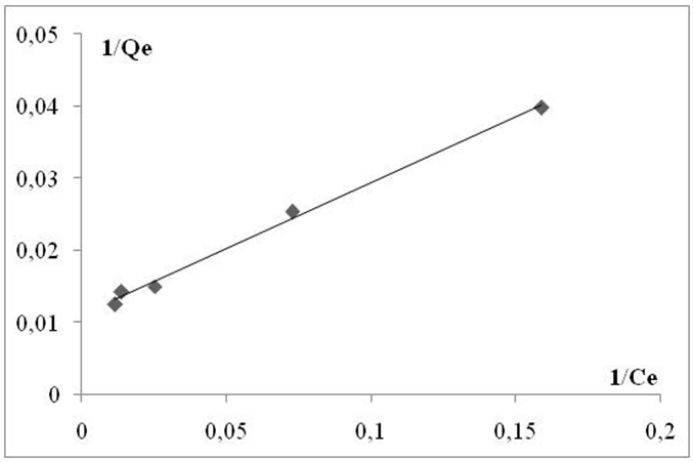


Figure 4: Langmuir Isotherm of the adsorption of methylene blue on Aeschynomene aspera m = 0.0615 g, pH = 5.5, T=25°C and 100 rpm.

b) Freundlich model

Freundlich proposes an empirical model which describes a physical adsorption of adsorbate molecules on heterogeneous adsorbent surface. Freundlich model is expressed by the following equation [33]:

$$\mathbf{Q_e = K_f\, C_e^{\,1/n}}$$

Where:

Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

C_e = the equilibrium concentration of adsorbate (mg/L)

K_f is adsorption capacity at unit concentration and *1/n* is adsorption intensity. Their values can be deduced from the linearization of the above equation:

$$\mathbf{Ln\ Q_e = f\ (Ln\ C_e)}$$

Adsorption is considered favorable when *n* value is higher than 1 and unfavorable if *n* value is lesser than 1.

From figure 5 which plots the linearization of Freundlich model for the adsorption of MB on AeAs, it can be deduced the values of n = 2.09, K_f = 11 mg/g and correlation coefficient R^2 = 0.947. Then, it might be noted that the Freundlich model does not fit perfectly the adsorption of MB onto AeAs. Neverless, the value of n = 2.09 reinforces the idea that adsorption is favorable as has been proved by Langmuir model.

c) Temkin model

Temkin proposes the following equation to describe the adsorption process:

$$\mathbf{Q_e = (RT/b)\ Ln\ (K_t\ C_e)}$$

Where, b is the heat of adsorption (J/mol) and K_t is the equilibrium bending constant (L/mg).

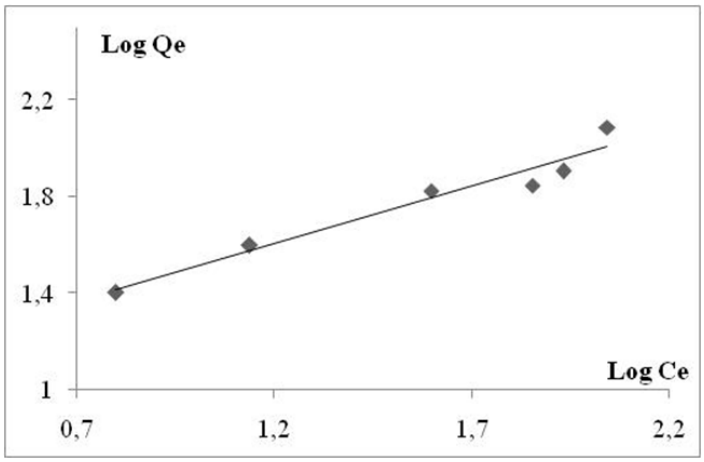


Figure 5: Freundlich Isotherm of the adsorption of methylene blue on Aeschynomene aspera m = 0.0615 g, pH = 5.5, T=25°C and 100 rpm.

The linearization of Temkin equation leads to the following formula:

$$\mathbf{Q_e = (RT/b)\ Ln\ K_t + (RT/b)\ Ln\ C_e\ [12]}$$

From the linearization of Temkin equation, as illustrated by figure 6, it can be deduced the values of correlation coefficient R^2 = 0.98, heat adsorption b = 52.60 J/mol and equilibrium bending constant K_t = 2.45 L/mg. It might be noted that the correlation coefficient is slightly lesser than unit. So, the results obtained from Temkin model might be used to explore the adsorption process.

The comparison of the results of Langmuir, Freundlich and Temkin models shows that the adsorption of MB molecules on the AeAs woods is rather governed by the Langmuir model. This model assumes that the solute - adsorbent interactions form a monolayer where the molecules of solute are sufficiently linked to adsorbent sites. These interactions might be assigned to ion - ion interactions between positive charges supported by dye molecules and negative charges supported by wood chains [17, 18].

3.4.2. Study of the adsorption kinetic of MB on AeAs

Kinetic study is widely used in the prediction of adsorption process. It allows calculating the rate constant and heat of adsorption. In literature, the main employed kinetics models are: pseudo - first order (or Largergren model), pseudo - second order (or Ho and Mc Kay model) and intra particle (or Weber and Morris model) [12, 31].

The model proposed by Lagergren, which describes the kinetic of the first - pseudo order, is based on the following equation:

$$\mathbf{Ln\ (q_e - q_t) = Ln\ q_e - k_1\ t}$$

Whereas, the model of Ho and Mc Kay, which interpreted the kinetic of the second - pseudo order, is illustrated by the following equation

$$\mathbf{t/q_t = 1/(k_2\ q_e^2) + t/q_e}$$

To describe the diffusion of adsorbent molecules from the bulk of the solution towards the adsorbent matrix (pores), Weber and Morris propose the following equation:

$$\mathbf{q_t = k_i\ t^{1/2}}$$

Where:

q_t : is the adsorption capacity at time t;
q_e: is the equilibrium adsorption capacity;
t: is the time in minutes;
k_1 : is the pseudo first rate constant;
k_2 : is the second - pseudo rate constant;
k_i: is the intra particle rate constant.

The applicability of each model was tested by the plotting of its equation. Model is considered appropriate to describe the adsorption process when the value of correlation coefficient (R^2) is higher than 0.99 and the theoretical results are close to experimental ones.

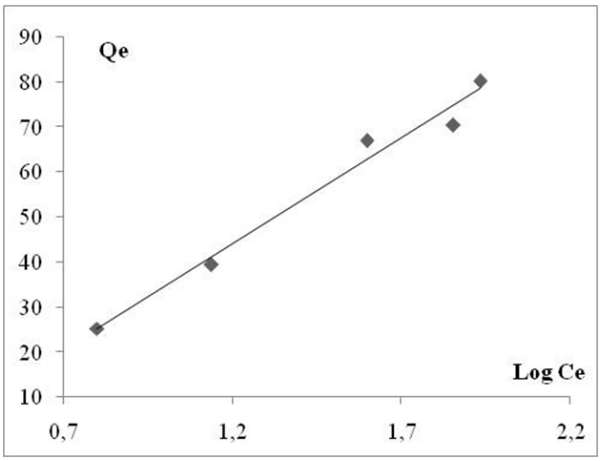


Figure 6: Temkin Isotherm of the adsorption of methylene blue on Aeschynomene aspera
m = 0.0615 g, pH = 5.5, T=25°C and 100 rpm

Figure 7 presents the kinetic plot of MB adsorption on AeAs according to pseudo first order; whereas Figure 8 shows MB adsorption according to pseudo second order.

Table 2 summarizes the kinetic parameters obtained from different kinetic models. It appears clearly that the values of correlation coefficient R^2 corresponding to pseudo second order was greater than 0.99 and the theoretical equilibrium adsorption (Q_e = 57 mg/ g) was very close to the experimental value (Q_e = 54 mg/g). So, the adsorption of MB on AeAs is well fitted by pseudo second order mechanism, rather than other models. Similar results were observed for some low cost adsorbents as wheat shells, *Eucalyptus sheathiana* bark, jackfruit peel and Gypsum [5, 12, 13, 17].

Table 2: Kinetics parameters deduced from pseudo 1st and 2nd orders and intra particle diffusion of methylene blue adsorption on Aeschynomene aspera at: C = 100 mg/L, pH = 5.5, T=25°C and 100rpm.

1er ordre			Diffusion		2ème ordre		
R^2	K_1	Q_e mg/g	R^2	K_i	R^2	K_2	Q_e mg/g
0.948	0.0008	4.03	0.824	0.446	0.999	2.0 10^{-4}	57.80

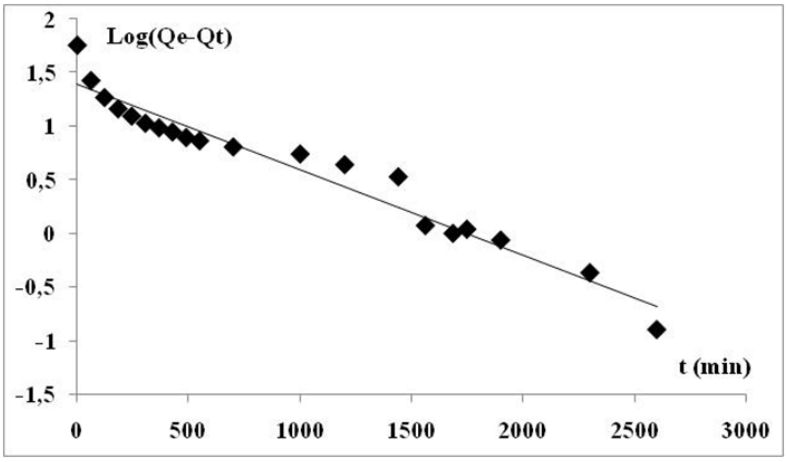


Figure 7: Pseudo 1rt order mechanism of adsorption of methylene blue on Aeschynomene aspera C = 100 mg/L, pH = 5.5, T=25°C and 100 rpm.

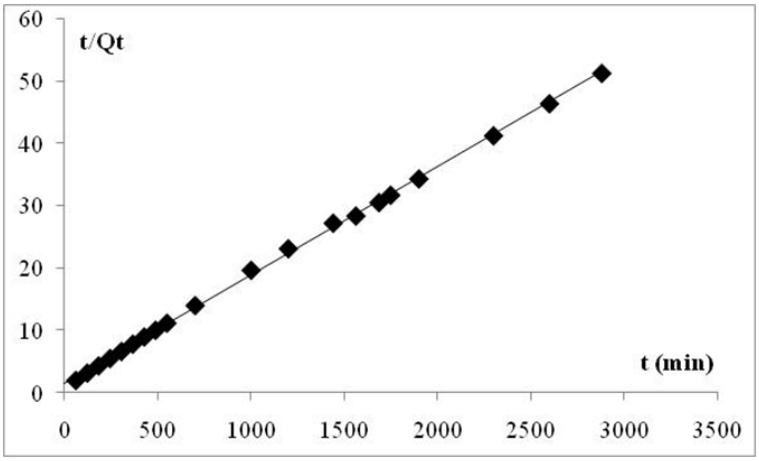


Figure 8: Pseudo 2nd order mechanism of adsorption of methylene blue on Aeschynomene aspera C = 100 mg/L, pH = 5.5, T=25°C and 100 rpm.

4. CONCLUSION

This paper describes the removal of methylene blue (MB) dye from aqueous solution by adsorption on the *Aeschynomen aspera* (AeAs) wood. Adsorbent properties such as ionic exchange capacity, swelling and porosity ratios and adsorption process were investigated. Results show that the maximum adsorption capacity of MB on AeAs is 91 mg/g and the adsorption process follows the Langmuir model, whereas the kinetic mechanism of adsorption is governed by the pseudo 2nd order.

Acknowledgements

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