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BIOSORPTION OF METHYLENE BLUE FROM WASTE WATER USING LEBANESE *CYMBOPOGON CITRATUS* (CITRONNELLE)

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Abstract

The objective of this study was to investigate the possibility of using Lebanese *Cymbopogon citratus* stem as an alternative adsorbent for the removal of methylene blue from aqueous solutions. Different parameters such as the effect of initial concentration, pH, adsorbent dose, contact time and temperature were studied. Maximum adsorption capacity (61%) of MB was obtained at PH=6 an initial concentration 200 mg/L after 24h and at 25 ˚C. The adsorption isotherm was better described by a Freundlich model rather than a Langmiur model. Based on these results, it can be concluded that the stems of Cymbopogon citratus is effective as an alternative adsorbent for MB remediation in waste water.

Keywords: Cymbopogon citratus, adsorption, Langmiur and Freundlich isotherm models

Introduction

Many industries use synthetic dyes and pigments that may find their way into natural waterways [Haddadian Z, 2013]. Reactive dyes, an anionic or cationic dye, are most commonly used due to their provision of bright colors, excellent color fastness, and easy application. However, many reactive dyes are toxic to organisms and may cause direct harm to aquatic life. Accumulation of these dyes in wastewater from industries such as textiles, paper, cosmetics, rubber, and plastics has been regarded as a significant source of water pollution [Umpuch C, 2013]. Discharge of colored wastewater without proper treatment can results in numerous problems such as chemical oxygen demand (COD) by the water body and an increase in toxicity. Currently, there are about 10,000 different commercial dyes and pigments exist and over $7x10^5$ tones of synthetic dyes are produced annually world-wide [Owamah HI, 2013]. Furthermore, dyes in waste water are difficult to remove because they are stable to light, heat and oxidizing agents. In short, they are not easily degradable [Jain R, 2008]. Moreover, their degradation products may be mutagenic and carcinogenic [Saha P, 2012]. Many dyes may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system [Khan TA, 2011]. Organic dyes are harmful to human beings; the need to remove color from wastewater effluents becomes environmentally important. It is rather difficult to treat dye effluents due to their synthetic origins and mainly aromatic structures, which are biologically non-degradable. Among several chemical and physical methods, adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater [Aksu Z, 2010]. Numerous treatment processes are now available for effluent discharged from industrial processes containing dyes as: adsorption [Wan Ngah WS, 2011], chemical oxidation[Wang S.A, 2008] electrolysis [Jin YZ,Zhang YF, 2003], biodegradation [Barragan BE, 2007], and photo-catalysis[Malekbala MR, 2012]. Among all the physical treatments, adsorption process has been reported to be the most effective method for water decontamination [Mohammed MA, 2014]. The removal of methylene blue from waste water needs great attention. In this present study, Lebanese *Cymbopogon citratus* has been utilized as an adsorbent for the removal of methylene blue from aqueous solutions. The adsorption data have also been correlated with adsorption isotherms and kinetics of adsorption has been studied to determine the efficiency of an adsorption process. Adsorption isotherm which includes Langmuir and Freundlich was used to correlate the adsorption data, kinetic and thermodynamic parameters were studied too.

Materials and methods

Preparation of Methylene Blue Solution

Methylene blue, a basic cationic dye, ($C_{16}H_{18}C_lN_3S.3H_2O$; M.W: 373.90), was supplied by UNI-CHEM and used as an adsorbate. Stock solution of 1000 ppm was prepared by dissolving an accurately measured weight in 1 L distilled water. The solutions for use in experiments were obtained by diluting the stock solution to the desired concentration.

Preparation and Characterization of Adsorbent

Citronnelle utilized in this work was collected from Bekaa valley East Lebanon. The collected plants were carefully washed with running water to remove impurities, and then washed with distilled water. The clean plants were dried at room temperature for 10 days then in an oven at 70 ^oC for 6 hours. The dried Citronnelle was grinded to a fine powder in a grinding mill to get a size of 0.25 mm. Fourier transformation infrared (FTIR) analysis using JASCO FT/IR-6300 spectrometer was applied to determine the surface functional groups interfering in the adsorption of methylene blue, where the spectra was recorded in the range of 4000 to 400 cm^{-1}.

Experimental methods

Batch experiments to study the capacity of Citronnelle to remove methylene blue from solution were carried out using a series of erlenmeyer flask of 50 mL capacity where 25 mL of methylene blue were mixed with 0.25 g of the adsorbent. The experiments were prepared to study the effect of initial methylene blue concentration, pH, contact time, adsorbent dose and temperature on adsorption of methylene blue from its solution. All the adsorption experiments were carried out at room temperature and the original pH of the solution except where the effect of temperature and pH was being investigated. The initial pH was adjusted with HNO_3 (0.1 M) or NaOH (0.1 M) solutions. At the end of each adsorption experiment, the adsorbent was removed by filtration through a (0.45 μm) filter paper, and the dye concentration at equivalence was analyzed using a UV visible spectrophotometer by monitoring the absorbance changes at λmax= 665 nm. The dye removal efficiency (R) and the amount of dye adsorbed per unit mass of adsorbent at time t (qt, $mg.g^{-1}$) and at equilibrium (qe, $mg.g^{-1}$), were calculated using the following equations:

$R (\%) = [(C0 – Ce)/C0]*100$

$qt = [(C0 – Ct)/m]*V$

$qe = [(C0 – Ce)/m]*V$

$C0$($mg.L^{-1}$): initial dye concentration

Ct ($mg.L^{-1}$): dye concentration at time t

Ce($mg.L^{-1}$): equilibrium dye concentration

qe($mg.g^{-1}$): amount of dye adsorbed onto the adsorbent at equilibrium
qt($mg.g^{-1}$): amount of dye adsorbed onto the adsorbent at time t
V (L): volume of the dye solution
m(g): mass of the adsorbent

Adsorption Isotherm

Adsorption isotherm is basically important to describe how solutes interact with adsorbates, and is critical in optimizing the use of adsorbents [14].

Langmuir Isotherm

It is based on the assumption that it predicts monolayer coverage of the adsorbed bate on the outer surface of the adsorbent. This model also suggests that there is no lateral interaction between the adsorbed molecules [Idris S, 2012]. Linear form of Langmuir isotherm is:

$1/qe=1/bqmCe + 1/qm$
Ce ($mg.L^{-1}$): equilibrium dye concentration
qe($mg.g^{-1}$): amount of dye adsorbed onto adsorbent at equilibrium
qm ($mg.g^{-1}$): maximum monolayer capacity of the adsorbent
b ($L.mg^{-1}$): Langmuir isotherm constant

Freundlich Isotherm

It is based on multilayer adsorption on heterogeneous surface. The linear form of Freundlich isotherm is:
$lnqe = lnKF + (1/n)lnCe$
KF ($L.mg^{-1}$): Freundlich constant indicating adsorption capacity
n: adsorption intensity

Results and discussion

When *Cymbopogon citratus* stem powder was tested for its ability to adsorb methylene blue from aqueous solution, initial pH = 4 was used for most experiments. The effects of the following experimental parameters (pH, initial concentration, contact time, temperature and the adsorbent dose) on adsorption were studied. The percentage of the uptake or adsorption of methylene blue was calculated using the following equation:

$$\%\, removal = \frac{Ci - Cf}{Ci} \times 100$$

Where:
$C_{o:}$ initial concentration (mg/L)
C_f: final concentration (mg/L)

The adsorption capacity is the concentration of methylene blue over the adsorbent mass and it was calculated based on the mass balance principle according to the following equation:

$$\text{qm (adsorption capacity)} = \frac{Co - Cf}{m} \times V$$

Where,
qm: amount of methylene blue per dry weight of *C.citratus*
V: volume of the reaction mixture (L)
m: mass of adsorbent used (g)
Co: initial concentration (mg/L)
Cf: final concentration (mg/L)

FT-IR analysis

The FT-IR spectrum of *C. citratus* was used to investigate the functional groups present on the plant that could be responsible for the removal of heavy metal species. The spectrum of the adsorbent was measured within the range of 400-4000 cm^{-1} wave number. The comparison of the FT-IR spectra has been done before and after loading with methylene blue. The *C. citratus* stems show a number of absorption peak that reflect its complex nature. Three peaks between 3300-3500 cm^{-1} are due to the presence of N- bond stretching. A peak at 2930 cm^{-1} is due to C-H stretching vibration. The absorption peak at 1750 cm^{-1} could be assigned to carboxyl group, 1140 cm^{-1} (between 1080-1210 cm^{-1}) to C-O stretch.

After adsorption, a broad peak at 3420 cm^{-1} corresponds to the overlapping of N- peak, also, a broad peak at 1750 cm^{-1}. This phenomenon may be attributed to the water molecule directly interacting with amide.

After methylene blue binding, a change of peak position occurs (3540-3500 cm^{-1}, 3500-3490 cm^{-1}, 3850-3800 cm^{-1}, 3000-2950 cm^{-1}, 1750-1730 cm^{-1}, 1100-1080 cm^{-1}, 550-540 cm^{-1}).

The shift in the wavelength corresponds to the change in the energy of functional groups that indicates the existence of methylene blue binding process done on the surface of *C. citratus* stem powder

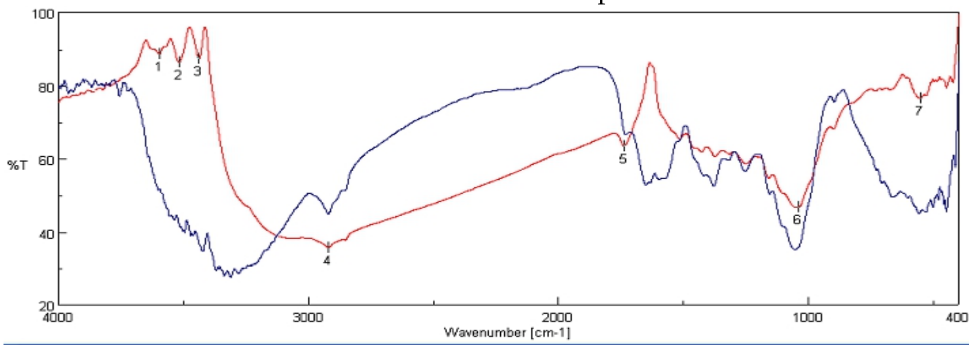

Figure 9: FT-IR of *Cymbopogon citratus* before and after adsorption

XRF-analysis

The XRF analysis spectrum has been done to show the metals composition in the stems of *Cymbopogon Citratus* .it was consisting of K, Ni, Nb, Mo, Sn (figure 2)

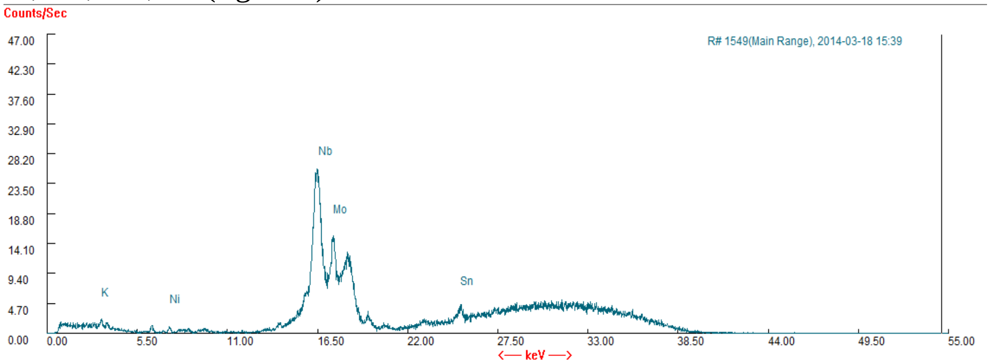

Figure 10 : XRF analysis of *Cymbopogon citratus***.**

Effect of Methylene Blue Concentration

To investigate the effects of the methylene blue concentration on the adsorption capacity, the process was carried out with initial methylene blue concentration between 100 and 400 mg/L while keeping the other four parameters constant. General increase in adsorption capacity of methylene blue with the increasing concentration. An increase in the initial methylene blue concentration from 100 to 400 mg/L, leads to an increase in the adsorption capacity of Citronelle as well from 9.54 to 37.65 mg/g respectively, and this can be attributed to an increase in the driving force for the mass transfer between the aqueous phases and the solid phase [Senthil Kumar P, 2010].

Adsorption of an organic pollutant, methylene blue two methods have been done that are different to each other by the contact time between the adsorbent and the adsorbate. *Cymbopogon citratus* was used for the adsorption of methylene blue under these conditions (ambient temperature, t = 24 hours, V / m = 0.5) where V is the volume of solution and m is the mass of the adsorbent. We note that the time chosen was beyond the equilibrium time (is the maximum efficiency of the adsorption of methylene blue and thus the minimum residual contents methylene blue) where beyond this time, removal efficiency decreases.

First method (ambient temperature, t = 24 hours)

pH Effect

The effect of the change in pH with fixing the other parameters (initial concentration of methylene blue = 200 mg/L, room temperature, t=

24 hours) appears in Figure .4. The percentage adsorption of methylene blue is maximal at pH= 6, which is 60.4%. When the (pKa = 3.8 of methylene blue) there is a competition of the ion with H^+ organo-cations to negatively charged sites. When pH> pKa, the conjugate acid concentration is lower. However the pH is an important parameter because it gives an indication on the forms in which the pollutant and the surface of the matrix exist, and therefore the nature of interactions.

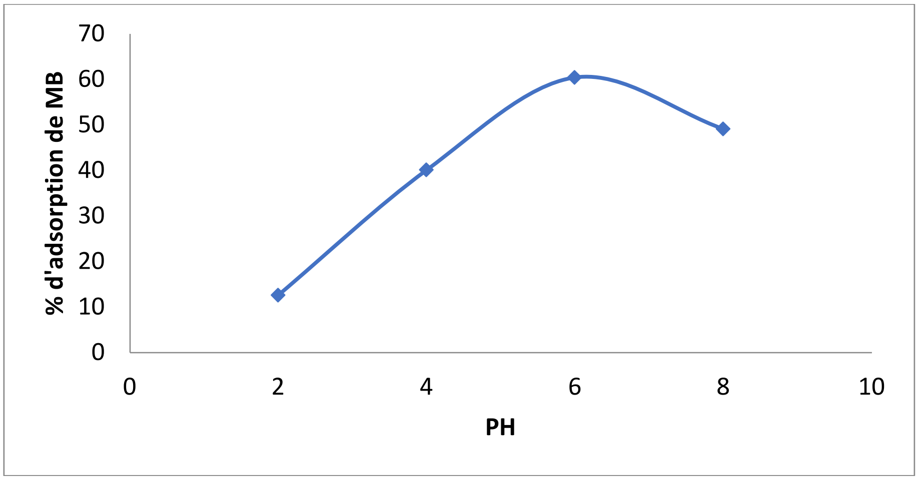

FIG 4

Concentration Effect

Figure 5 shows that the amount of methylene blue adsorbed increases with the increase in the concentration to reach 54.07 mg/g when the concentration is 40 mg/L, then, becomes constant, which is due to the saturation of the surface of the adsorbent.

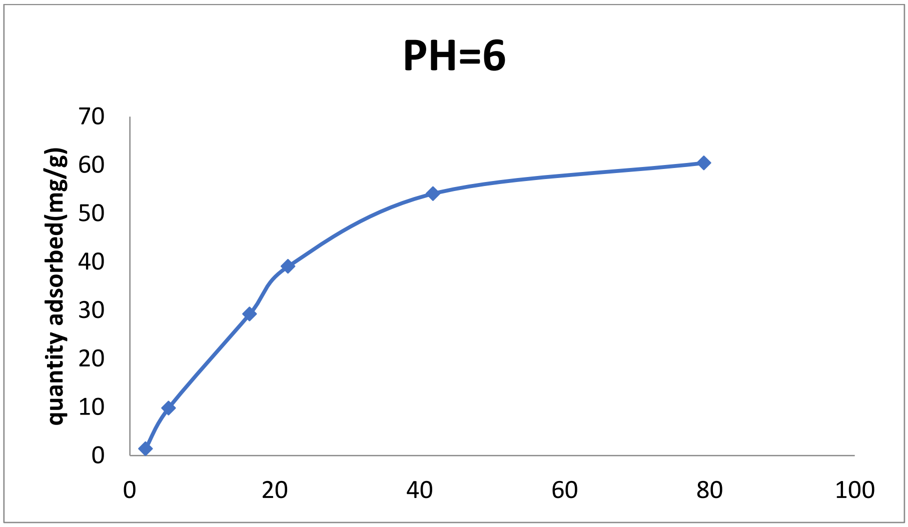

Figure 5: effect of variation of concentration of methylene blue.

Effect of the adsorbent mass

The change in the dose of the adsorbent shows the same shape of the curve where the amount of methylene blue adsorbed increases and then it does not evolve. This behavior may be due to the number of adsorption sites, which increases with the increase in the amount of adsorbent and the number of sites becomes stable which explains the amount of methylene blue becomes constant. We note that the amount of methylene blue adsorbed is important when the dose of the adsorbent is 25 mg.

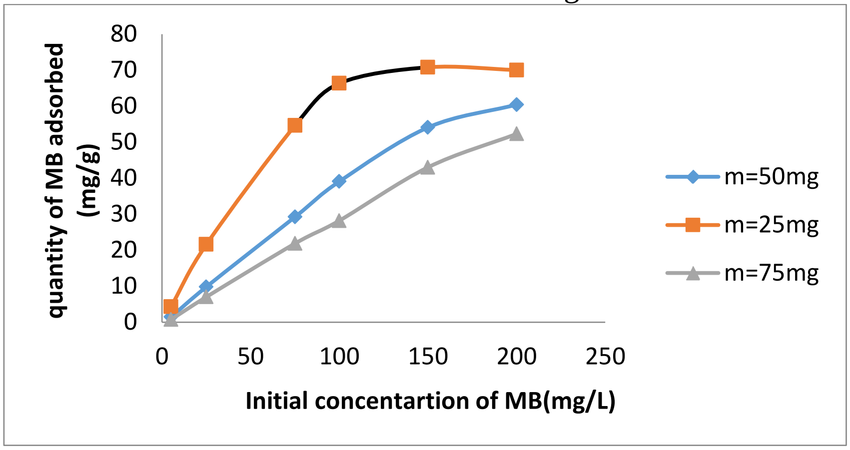

Figure 6: effect of variation of dose of the adsorbent.

As long as the amount of adsorbent added to the dye solution is low, the cations of the dye can easily access the adsorption sites. The addition of adsorbent can increase the number of adsorption sites but the cations of the dye have more difficulties in approaching these sites because of dimensions.

A large amount of adsorbent creating complexes of particles leads to a reduction of the total adsorption area and therefore a decrease in the amount of adsorbate in the adsorbent unit.

Second method: (t = 1 hour)

Cymbopogon citratus is used for the adsorption of methylene blue under these conditions (ambient temperature, time = 1 hour, V / m = 1) where V is the volume of solution and m is the mass of the adsorbent.

Initial concentration effect of MB

Fig 7 shows the variation of the adsorbed amount of methylene blue with the variation of the initial concentration of methylene blue in fixing the other parameters (T= 25 °C, pH= 6, t= 1 hour). This quantity increases rapidly with the increase of the initial concentration then it continues to increase slowly to 37 mg/g when the concentration of methylene blue was 500mg/L.

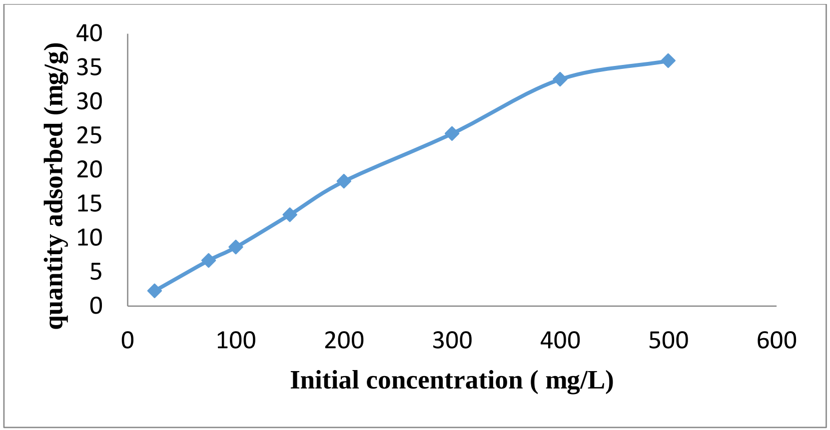

Figure 7: effect of varying the initial concentration.

pH Effect

In order to evaluate the effect of this parameter, five experiments were realized for pH between 2 and 10. This parameter is adjusted with HCl (0.1 M) or NaOH (0.1 M). The initial concentration of methylene blue, the stirring speed, temperature and contact time were kept constant. According to the obtained results, we note that the methylene blue has the best adsorption at pH= 6. At pH<6, the variation of the capacity is slightly different. This can be explained by the fact that at low pH values, the surface of the adsorbent would be surrounded by the H^+ ions which reduces the interaction of methylene blue ions (cationic pollutant) with the adsorbent sites.

A moderate pH (near 6), the H^+ concentration decreases, which leads to a good interaction between the ions of the dye and the surface sites. In addition, the increase in the adsorbed amount of methylene blue in the acid medium is due to the fact that the molecule contains amino groups which are ionized by quaterization with H^+, which leads to an increase of the amount adsorbed [16].

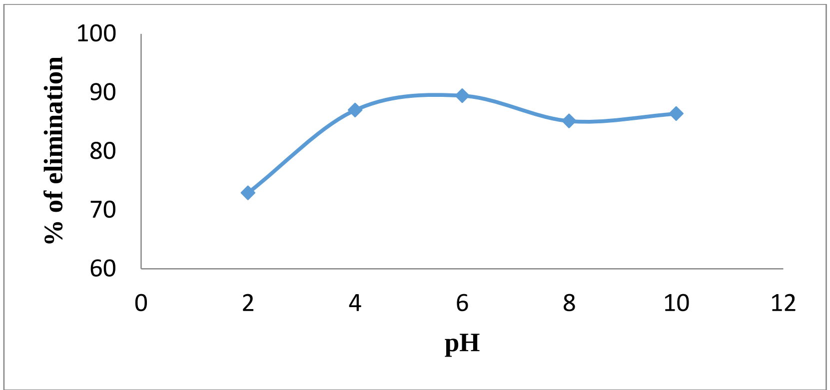

Figure 8: effect of varying pH on the adsorption of.

Effect of the dose of the adsorbent

Fig 8 shows that the amount of adsorbed dye increases with the addition of the adsorbent to 92.68%. From an amount of 0.5 g, the amount of dye approximately remains constant. This behavior may be due to the number of adsorption sites, which increases with the amount of adsorbent and then, from 0.5 g of the adsorbent, the number of sites becomes stable [De Sa FP, 2013], which probably indicates the presence of another type of interaction between the dye and the *Cymbopogan citratus*. It is about a competition between the parts retaining dye fractions and the free parts of the adsorbent that attract the latter, making it back into solution [Alencar WS, 2012].

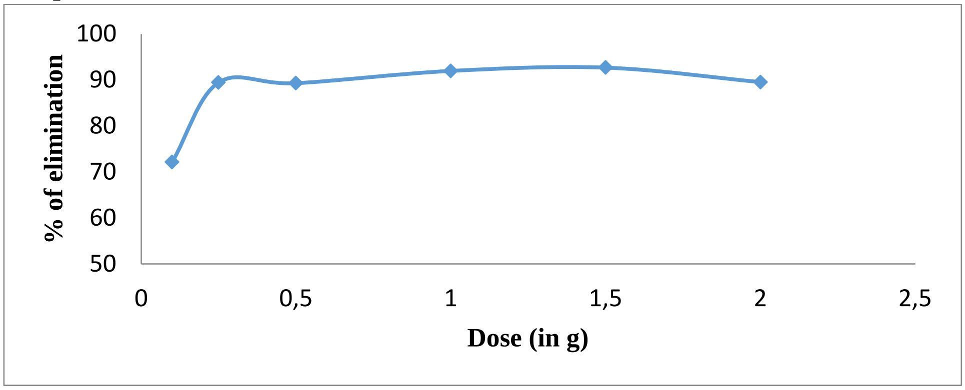

Figure 8: effect of adsorbent dosage on the adsorption.

Temperature Effect

The temperature is a parameter which affects the adsorption process. The temperature was adjusted between 0 and 60 °C. The temperature has a double effect on the adsorption mechanism. An increase in temperature allows an increase in the kinetics of the adsorbate. This means that the particles are moving more quickly to the surface so that they are adsorbed. However, the adsorbed species can win enough of the temperature of the system and be desorbed on the same rhythm.

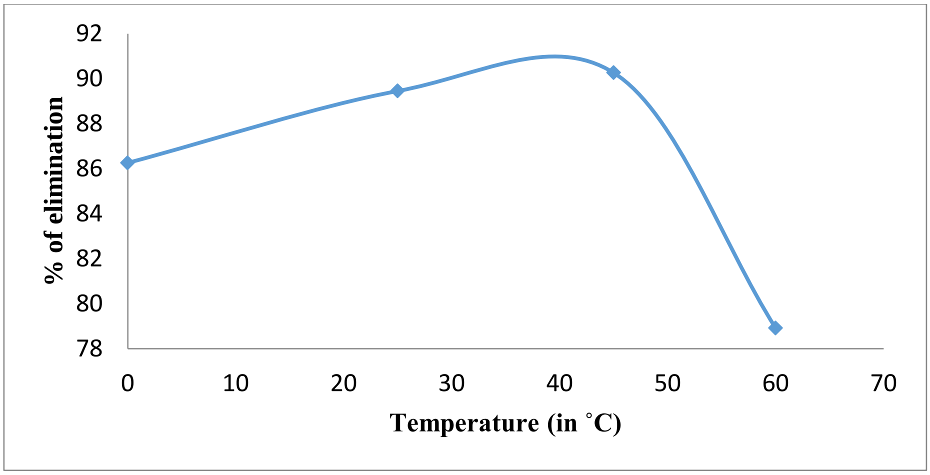

Figure 9: effect of variation of temperature on the adsorption of methylene blue.

Contact time Effect

Fig 10 shows the variation of the percentage of methylene blue adsorbed as a function of contact time. We note that this percentage decreases slowly to a minimum in two hours (50%) and then it starts to increase to 93.66% at t= 3 hours. The results show that the time of equilibrium is 30 minutes.

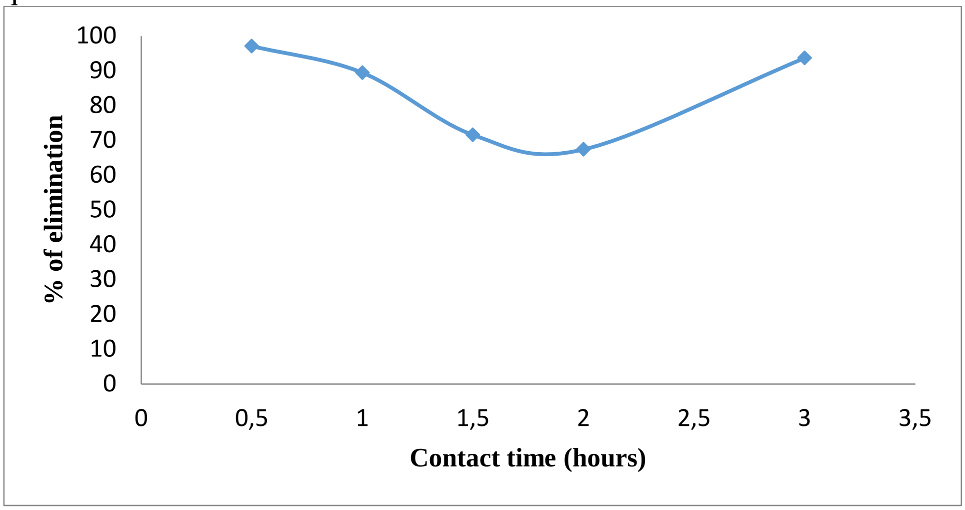

Figure 10: effect of varying the contact time on the adsorption.

Isotherm Methylene Blue

- Langmuir isotherm:

This graph shows the variation of $1 / q_e$ versus $1 / C_e$. A straight line is obtained with $R^2 = 0.998$.

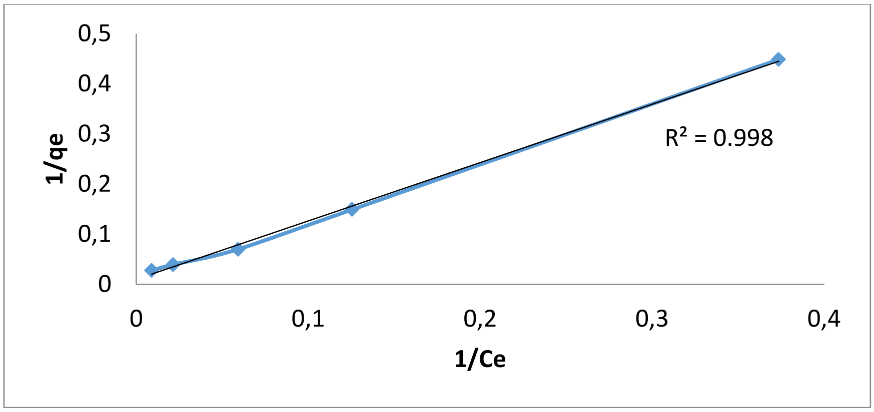

Figure 11: Langmuir isotherm

Langmuir constant:

	q_{max}	K_L	R_L
MB	111.11	0.0077	0.64

Table 1

R_L = 0.64, concentration range (5 and 200 mg/L). R_L is between 0 and 1 then the biosorption is favorable.

- Freundlich isotherm:

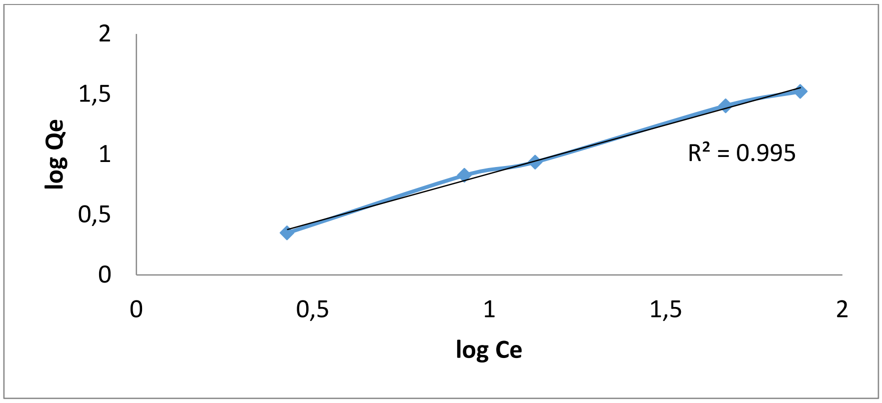

Figure 12: Freundlich isotherm.

Freundlich constant:

	K_F	n	R^2
MB	1.0690	1.23	0.995

Table2

Since n> 1, then, it is a physical adsorption.

Conclusion

The adsorption of heavy metals by the Lebanese *Cymbopogon citratus* was studied by varying several parameters: initial concentration of metal ion dose of the adsorbent, contact time, pH and temperature. Characterization of *Cymbopogon citratus* was made by XRF, FT-IR and particle size. The adsorption of a cationic dye (methylene blue) was studied, and the results showed a better adsorption of the dye. Isotherms were described by the model of Langmuir and Freundlich. Langmuir, adsorption is favorable for the metal ions of Cr (VI) and Cu (II) but is not favorable for Pb (II). Similarly, the adsorption is favorable for methylene blue. According Freundlich adsorption of Cr (VI) and Cu (II) is physical since $n > 1$, but the chemical adsorption is for Pb (I) since $n < 1$. For methylene blue, adsorption is physical. Arguably the *Cymbopogon citratus* rod can be considered a reliable adsorbent with a low cost. It is very effective in removing heavy metals from aqueous medium and even for organic pollutants such as methylene blue. This method can be used in the substituent in water treatment by the activated carbon expensive and requires a significant energy input for its manufacture, thus making very high cost of treatment of the cubic meter of water. This study may continue the study of the effect of *Cymbopogon citratus* on various heavy metals like Zinc, Magnesium, Nickel, Mercury ... and certain organic pollutants.

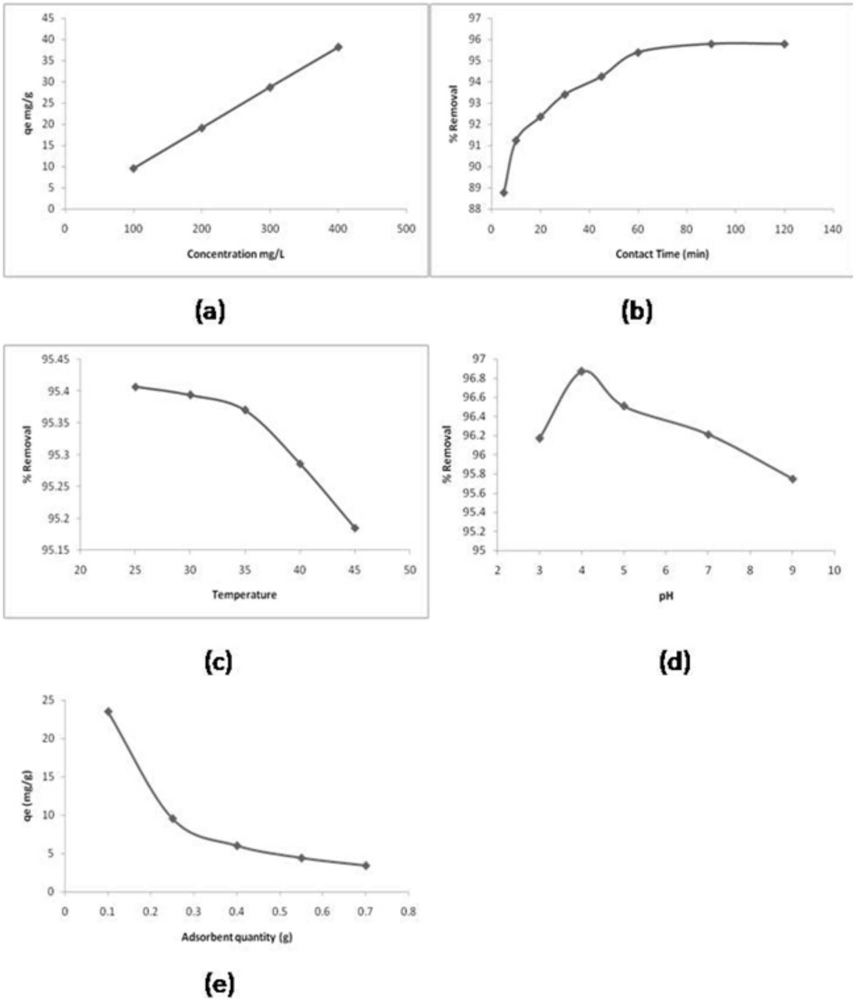

Figure 3: Effect of (a) Concentration, (b) time, (c) Temperature, (d) pH and (e) dose on Adsorption of MB

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