Characterization of the Corallina Elongata Alga and Study of its Biosorption Properties for Methylene Blue

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Summary: Biosorbents can be an alternative to activated carbon. They are derived from agricultural by-products or aquatic biomass. They are low cost and they may have comparable performances to those of activated carbon. The present study focuses on the characterization of the Corallina Elongata (CE) alga and its adsorption performance for Methylene Blue (MB), this alga is found in abundance at the Mediterranean coast of the city of Jijel in eastern Algeria. The dried alga was characterized using various characterization techniques such as DTA, TG, FTIR, XRD, SEM and EDX, which showed that the material consists essentially of a calcite containing magnesium. Batch adsorption studies were carried out and the effect of experimental parameters Such as pH, initial dye concentration, temperature, adsorbent dose and contact time, on the adsorption of MB was studied. The kinetic experimental data were found to conform to the pseudo-second-order model with good correlation and equilibrium data were best fitted to The Langmuir model, with a maximum adsorption capacity of 34.4 mg/g. The adsorption isotherms at various temperatures allowed the determination of certain thermodynamic parameters (ΔG, ΔH and ΔS). Finally, the adsorption results showed a good affinity between CE and MB with a high adsorption capacity.

Keywords: Alga, Biosorption, Corallina elongata, Isotherm, Dye.

Introduction

The synthetic coloring agents are organic substances used in numerous branches of industry. They are also found in quite domains and especially in the textile, paper industry, rubber, plastic, leather, cosmetics, and pharmaceutical and food industries. The presence of these substances in the effluents of waste water must be handled before rejecting them in the environment [1, 2], because most of these coloring agents are toxic, allergic, skin irritating and mutagenic and / or carcinogenic [3, 4]. The main conventional methods used to decontaminate waters are based on the membrane separation techniques [5-7], the reverse osmosis [8], the biological processing [9] and the adsorption [10]. The latter, is one of the most important methods of waste water treatment; it is based on the use of the activated carbon as adsorbent because of its excellent properties of adsorption, but the high cost of activated carbon has prompted several researchers to find other low-cost adsorbents for the elimination of coloring agents from contaminated water, for example some few inexpensive biosorbents are used to eliminate the cationic dye, the methylene blue, including yellow passion fruit waste [11], bagasse [12], neem (azadirachta indica) leaf powder [13], posidonia oceanica [14], coffee husks [15], papaya seeds [16] and brazilian pine-fruit shell [17]. The biosorption consists in using the dead or inert biomasses such as bacteria, industrial and agricultural waste as well as seaweeds, to hold by adsorption various contaminants (heavy metals, pesticidal, coloring) present in liquid or gaseous effluents. Among the biomasses, algae have the advantage of being very inexpensive compared to other commercial adsorbents, such as activated carbon. They are also abundant and renewable. In addition, they have active sites on their surface such as hydroxyl, carboxyl, amino, sulfhydryl and sulfonate, which are important in adsorption mechanisms [18, 19].

In this work we are interested in a mediterranean red seaweed, the corallina elongata, from the East of Algeria (Jijel city), at first the study concerned its characterization by various methods: TDA, TGA, FTIR, XRD, SEM and EDX, then we studied the adsorption of methylene blue in aqueous solution by varying diverse parameters as pH, temperature, Initial concentration of methylene blue and the mass of adsorbent.

Experimental

Adsorbate

The pollutant targeted in this study is the cationic dye methylene blue (MB), purchased from Sigma Aldrich with a formula: $C_{16}H_{18}ClN_3S$, its Characteristics are summarized in Table-1.

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Table-1: Properties and characteristics of MB.

Chemical name (IUPAC)	Dimethylamino-3,7 phenazathionium chloride
Molecular weight ($g.mol^{-1}$)	373.90
Molecular volume ($cm^3.mol^{-1}$)	241.9
Molecular diameter(nm)	0.8
Chemical Structure	

A stock solution of 1000 $mg.L^{-1}$ was prepared by dissolving the appropriate amount (1000 mg) of MB in one liter of distilled water. The working solutions were prepared by diluting the stock solution with distilled water to give the appropriate concentration of working solutions. The pH of the solution was adjusted by adding either 0.1 M HCl or 0.1 M NaOH respectively.

Table-1: Properties and characteristics of MB.

Preparation and characterization of the Alga

The corallina elongata alga used in this study was collected at the coasts of Jijel in eastern Algeria. The seaweed was washed several times with tap water to remove adhering dust, impurities as well as NaCl until clear wash water was obtained. Finally it was rinsed with distilled water and dried in oven at a temperature of 105 °C. After grinding, the sample was further dried in an oven and then sieved through a stack of sieves of different mesh openings. The fraction with a particle size between 80 μm and 100 μm was selected for the studies.

X-ray diffraction (XRD) experiments were performed with a D8 Advance Bruker AXS diffractometer with CuKα radiation equipped with a curved graphite monochromator. The data were collected in the 2θ range of 10–80° with a step size of 0.03° and a count time of 2 s per step. Thermal analysis of the sample was carried out using a NETZSCH STA 449 C device, under a nitrogen flow at the rate of 25 $mL.min^{-1}$ and a temperature range from room temperature to 1000 °C. Characterization by Fourier transform infrared spectroscopy was performed using SHIMADZU FTIR apparatus 84005. FTIR spectra were scanned between 4000 and 400 cm^{-1}. Characterization of morphology and microanalysis were performed by SEM (Scanning Electron Microscopy) on a JEOL JSM-6010LV instrument, equipped with an energy-dispersive X-ray spectroscopy (EDX) unit.

Batch adsorption and equilibrium tests

Adsorption measurements were determined, by batch experiments of known amount of adsorbent, with 50 mL of aqueous MB solutions of known concentration, in a series of 250 mL Erlenmeyer flasks. The mixture was shaken at a constant temperature (25 °C) using thermo line scientific orbital shaker incubator at 180 rpm. The dye concentration was measured by a double beam UV-VIS-NIR spectrophotometer (Shimadzu, Model UV-3150, Japan) at 664 nm. Each experiment was duplicated under identical conditions.

At predetermined time, the flasks were withdrawn from the shaker, and after the centrifugation of the mixture (adsorbent-adsorbate), the solution was analyzed on the UV visible, by measuring the absorption of the supernatant at the wavelength that correspond to the maximum absorbance of the methylene blue (664nm). The residual dye concentration in the solution was calculated from the methylene blue calibration curve.

Adsorption experiments were conducted by varying initial solution pH (3-11), adsorbent dose (10-100 mg), initial dye concentration (10-120 mg/L), and temperature (30, 40 and 50 °C), under the aspect of adsorption kinetics, adsorption isotherm, and thermodynamic study.

The amount (q_t) of dye adsorbed onto CE biomass at time t was calculated by the following relationship [20];

$$q_t = (C_0 - C_t) * (V/m) \quad (1)$$

where q_t is the amount of adsorbed dye at any time t ($mg.g^{-1}$), C_0 is the initial dye concentration ($mg.L^{-1}$), C_t is the concentration of dye at any time t, V is the volume of solution (L) and m is the mass of carollina elongata (g).

Results and discussion

Characterization

XRD

The X-ray diffraction results presented in Fig. 1 show that all the peaks coincide with those of calcite containing magnesium (Ca, Mg)CO_3 (JCPDS 43-0697), which is indexed in the trigonal system with the R-3c space group (No. 167) and the following lattice parameters: a = 4.942 Å and b = 16.85 Å, proving that the corallina elongata alga is a good source of calcium carbonate.

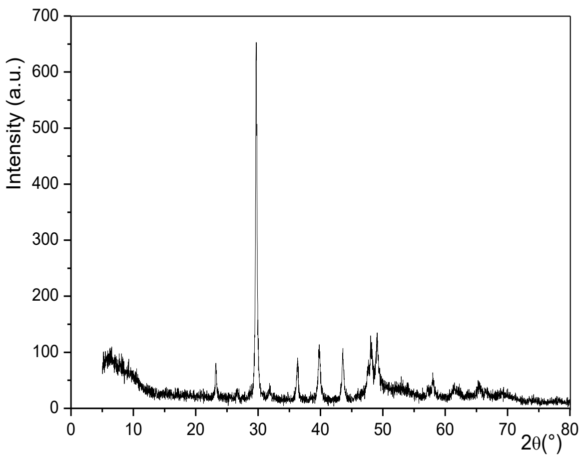


Fig. 1: X-ray diffraction pattern of the corallina elongata alga.

DTA and TG

Thermal analysis (Fig. 2) showed that the sample had different weight losses between room temperature and 1000 °C. However, there remains a large amount of the material after treatment at 1000 °C (about 50 %), proving its mineral character. In Fig. 2, we see three weight losses: the first loss happens around 110 °C accompanied by an endothermic peak, which corresponds to the loss of water physically adsorbed, the second loss takes place at 450 °C and is chemically related to adsorbed water, the most important loss (43 %) at 800 °C corresponds to the decomposition of $(Ca,Mg)CO_3$ with an endothermic peak [21], indicating the release of CO_2 according to the following reaction:

$$(Ca,Mg)CO_3(s) \rightarrow CaO(s)+MgO(s) +CO_2(g)$$

Beyond the temperature of disappearance of CO_2, it's noticed that the mass remains unchanged without any peak, which proves that the entire carbonate is converted into CaO and MgO with the disappearance of all the CO_2.

Infrared Spectroscopy

The infrared spectrum (Fig. 3) confirms the thermal analysis and X-ray diffraction; indeed, it confirms that the corallina elongata, consists mainly of calcium carbonate, the characteristic bands are 1432, 1789, 1084, 869 and 710 cm^{-1}, which correspond to different vibrational modes of the calcium carbonate molecule [22]. Other bands at 616 cm^{-1} and 1150 cm^{-1}, characterize the sulfate ions [23]. All these chemical bonds are favorable factors for the adsorption, they testify to the richness of the alga surface by active sites.

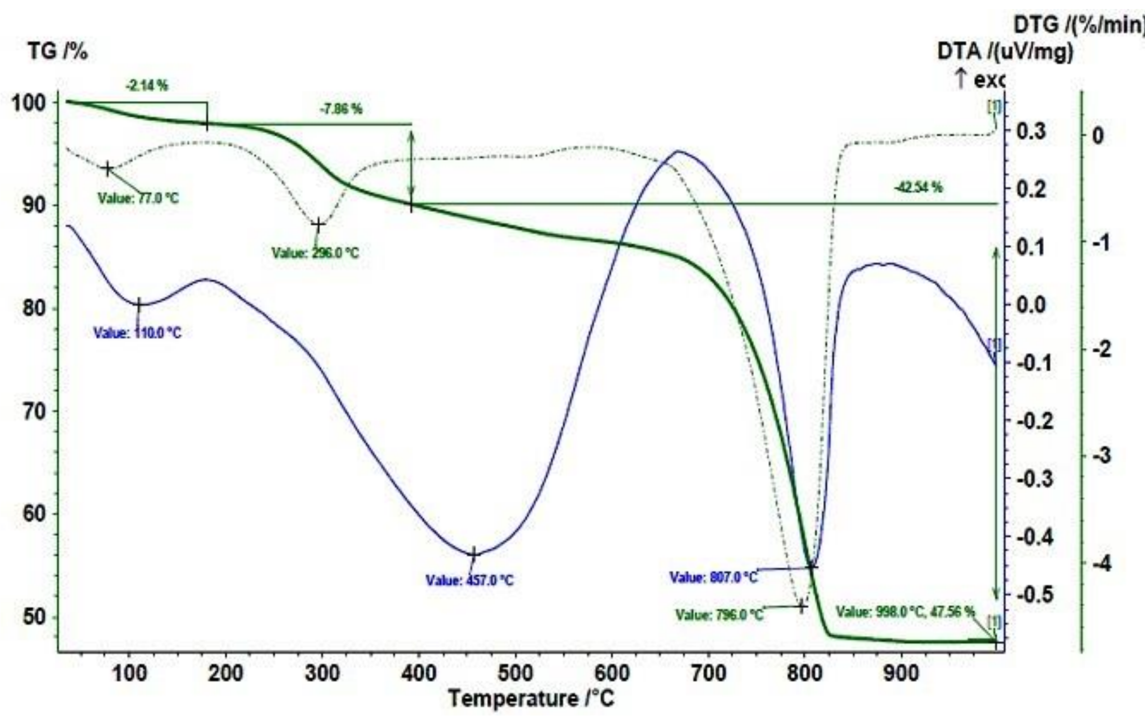


Fig. 2: DTA, DTG and TG curves of the corallina elongata.

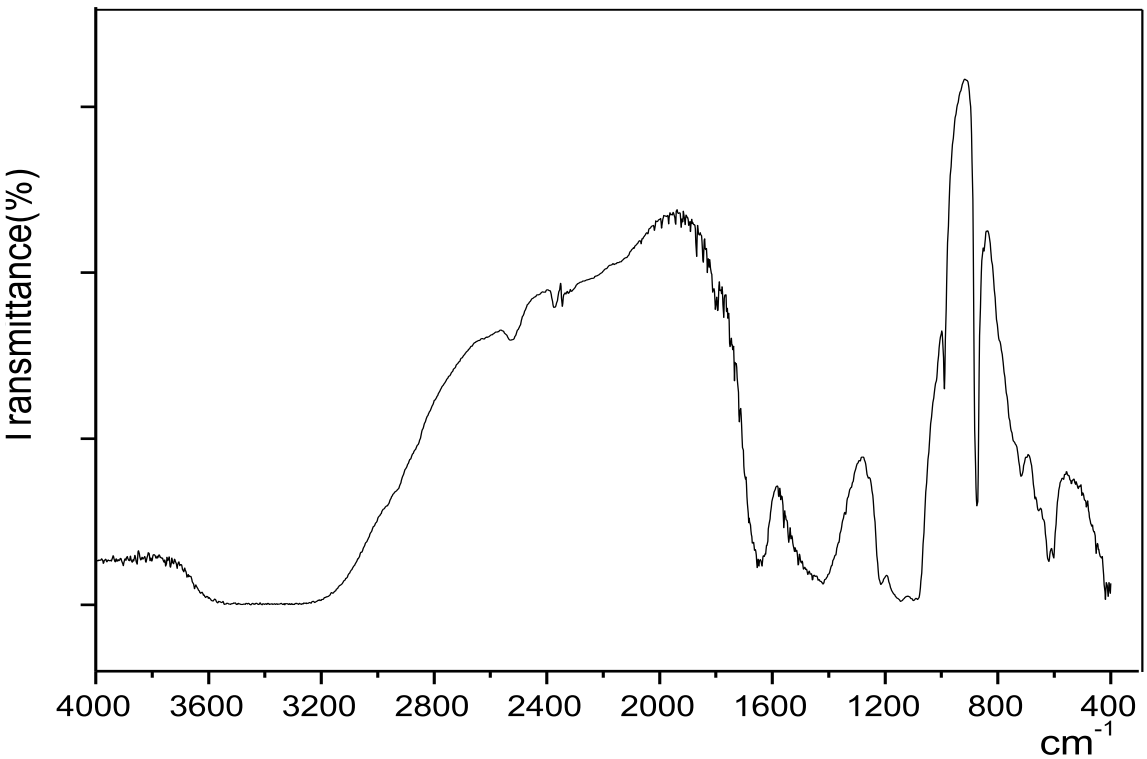


Fig. 3: FTIR spectrum of the corallina elongata.

Chemical Analysis and SEM

The chemical analysis (EDX) (Table-2) shows that the corallina elongata alga contains important quantities of calcium, carbon, magnesium and oxygen, which once again confirms that the alga is essentially a calcite containing magnesium, there is also some traces of other elements such as silicon, potassium, sulfur; this allows us to affirm the existence of sulfates.

Table-2: EDX data for the corallina elongata.

Element	Weight%
O	47,72
C	11.43
Na	0.36
Mg	3.62
Si	0.09
S	0.69
Cl	0.29
K	0.55
Ca	35,25
Total	100.00

The SEM micrographs of Fig. 4 show the general aspect of grains whose average size is 50 µm. We also distinguish in grains, highly ordered pores of uniform shapes, with a size of 5 µm.

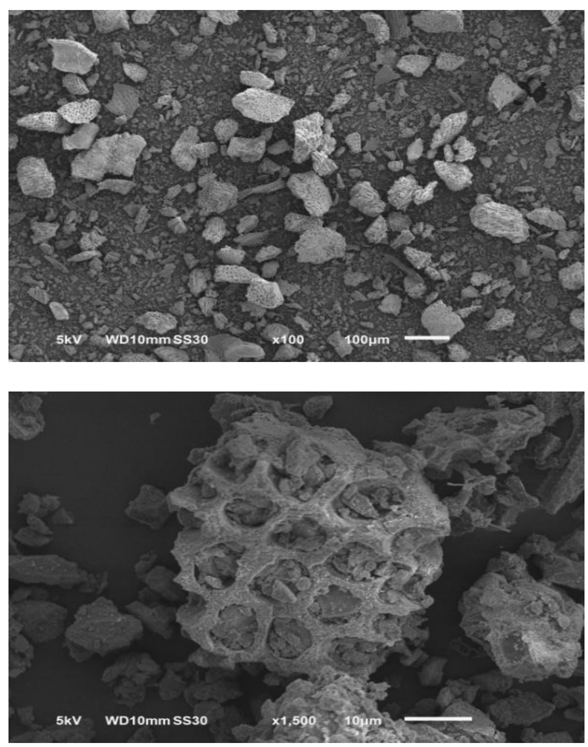


Fig. 4: SEM micrographs of the corallina elongata.

Adsorption Study

Effect of pH

The effect of initial pH on the adsorption amount of MB onto CE is studied at 25 ˚C, agitation speed 180 rpm, and 50 mg/L MB initial concentration, at different pH value (3-11), for 3 hours. The results in Fig. 5 showed that the adsorption yield of MB increases from 53 % to 84 % with increasing pH from 3 to 11.

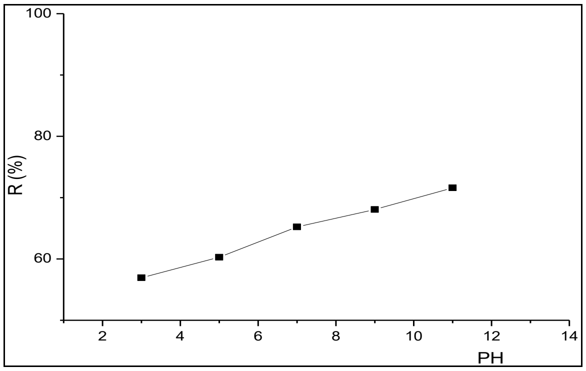


Fig. 5: Effect of the initial pH on MB removal.

At lower pH, the amount of adsorption was minimal, due to the richness of the solution by H^+ ions competing with the dye cations to the CE adsorptions sites.

At higher pH value (9-11) the MB adsorption yield was maximun and almost constant, this can be explained by the electrostatic interaction between the surface charge of the CE, which became negatively charged at higher than its pH of zero charge (pH_{PZC} = 9), with the positively charged MB dye. A similar result was observed for the adsorption of Methylene blue on Posidonia oceanica fibers [14], and the yellow passion fruit waste [11].

Fig. 5: Effect of the pH of the solution on the MB removal from the aqueous solution.

Effect of adsorbent mass

The effect of adsorbent amount on adsorption efficiency of MB onto CE was studied with changing the adsorbent mass from 10 mg to 100 mg, at temperature 25 ˚C, solution pH (9), 180 rpm and 50 mg/L MB initial concentration. In Fig. 6, the adsorbent efficiency of MB increases slightly (from 48 % to 49 %) when the adsorbent amount increases from 10 to 30 mg, this can be explained by the fact that the adsorbent amount is still insufficient to accommodate all the molecules of the adsorbate. In the other hand, it appears clearly that the effect of the adsorbent amount becomes more important between 30 mg and 100 mg (the efficiency increases from 49 % to 62 %); this can be explained by the increase of adsorption sites when the adsorbent amount becomes important.

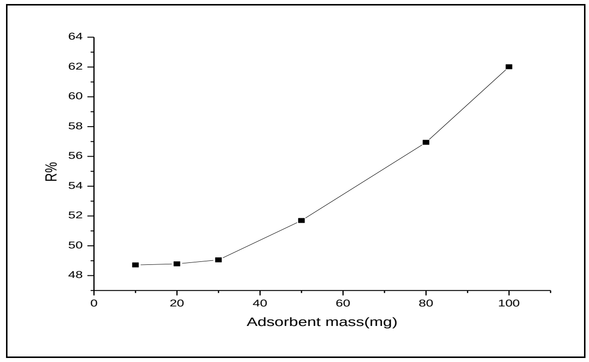
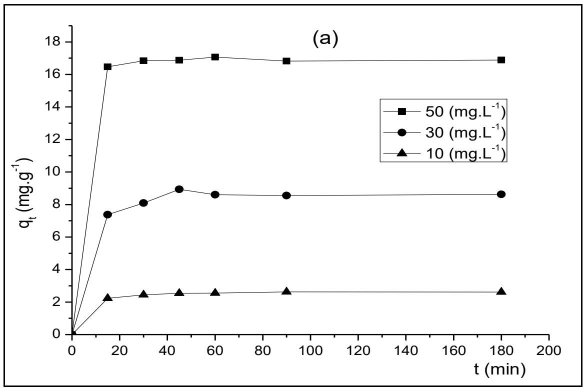


Fig. 6: Effect of the adsorbent mass on MB removal.

Determination of equilibrium time

Fig. 7a shows the extent of dye adsorption as a function of time and initial concentrations. We can affirm the following:

- Equilibrium is reached after 60 minutes with a maximum retention rate of 67.76 % for all the initial concentrations studied.
- The amount of MB adsorbed per unit mass of alga increased from 2.22 to 16.87 $mg.g^{-1}$ with increasing MB concentration from 10 to 50 $mg.L^{-1}$.
- Kinetic experiments indicated that adsorption of MB on CE followed three-step processes, especially for high initial concentrations: a rapid initial adsorption, followed by slower uptake of MB and finally no significant uptake. The first step is attributed to the instantaneous use of the most readily available active sites on the adsorbent surface (bulk diffusion). Second step, exhibiting additional adsorption is attributed to the diffusion of the adsorbate from the surface macro-pores of the adsorbent (pore diffusion intra-particle diffusion) stimulating further movement of MB molecules from the liquid phase to adsorbent alga surface [14]. The last stage is an equilibrium stage [16]. The rapid kinetic has a very important economic effect for the adsorption of water pollutants [24, 25].



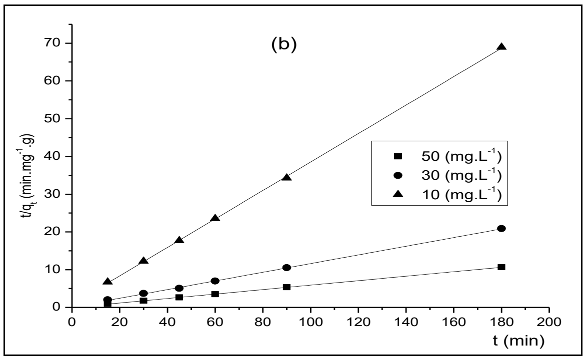


Fig. 7: Kinetic plots; (a) Effect of contact time on the adsorption of MB, (b) Pseudo-second order kinetic model.

To better describe the kinetics, we used the kinetic laws of the pseudo first order and the pseudo second order, represented by relations (2) and (3) respectively:

$$Ln(q_e - q_t) = Ln(q_e) - K_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (3)$$

The pseudo first order model is not verified by our results, whereas the pseudo second order model applies perfectly (Fig.7b). The experimental adsorption capacity (16.88 $mg.g^{-1}$ for $C_0 = 50$ $mg.L^{-1}$) coincides with that obtained by modeling (16.89 $mg.g^{-1}$), with a correlation factor R^2 = 0.999. The pseudo-second order rate constant decreases from 0.3638 to 0.0593 ($g.mg^{-1}.min^{-1}$), with increasing initial concentrations from 10 to 50 ($mg.L^{-1}$); this behaviour is caused by increasing competition between molecules on the adsorption sites, but at low concentrations this competition does not exist. Similar phenomena have been found for MB adsorption on Hazelnut shell [26], Tea waste [27], coir pith carbon [28], cedar sawdust and crushed brick [29], cadmium ferrite [30], sepiolite [31] and wheat shells [32].

Adsorption isotherm at room temperature

The adsorption isotherm of MB on the corallina elongata at room temperature is shown in Fig. 8; we represent on the abscissa axis, the residential concentration in the equilibrium solution C_{eq} ($mg.L^{-1}$) and on the ordinate axis, we represent the adsorbed quantity q_e ($mg.g^{-1}$), which was determined by the following formula:

$$q_e = (C_0 - C_{eq})\frac{V}{m} \quad (4)$$

where:

q_e: Adsorbed quantity ($mg.\ g^{-1}$), V: volume of the solution (L), m: adsorbent mass (g), C_0: initial concentration of the adsorbate ($mg.L^{-1}$), C_{eq}: residential concentration of the adsorbate at equilibrium ($mg.L^{-1}$)

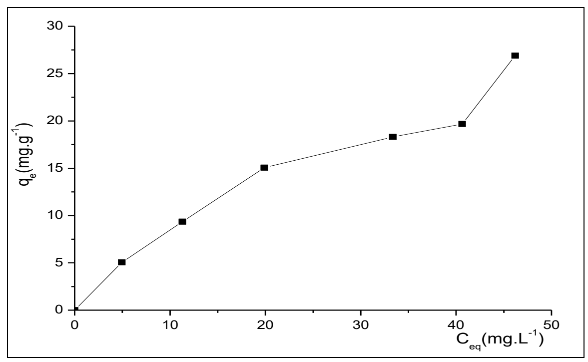


Fig. 8: Adsorption isotherm of MB on the corallina elongata at 25°C temperature.

According to Giles et al classification, Fig. 8 shows that the adsorption isotherm of MB on corallina elongata is the L-type (called Langmuir type), where the shape of the adsorption isotherm means that there is no strong competition between the solvent and the adsorbate to occupy the adsorption sites [33].

Also the description of the adsorption isotherms was carried out by applying the models of Freundlich and Langmuir (Fig. 9) [33, 34]. The Langmuir model describes the adsorption behavior of MB on CE better than the Freundlich model. where the linear form of the Langmuir model, represented in Fig.8b coincides better with the experimental results, giving a maximum adsorption amount of 34.42 $mg.g^{-1}$ with a correlation coefficient R^2 exceeding 0.99.

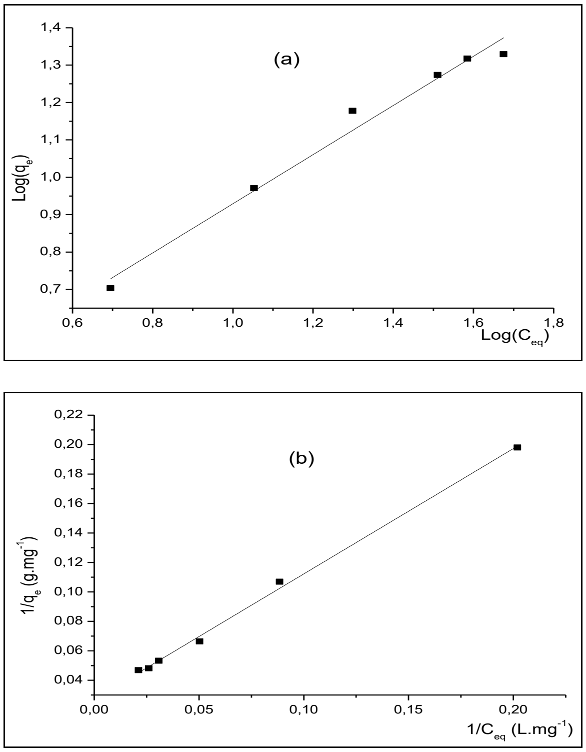


Fig. 9: Linearization of the isotherm using Freundlich (a) and Langmuir (b) models.

A comparison of corallina elongata to other low cost adsorbents, for methylene bleu adsorption, is given in Table-3. It appears clearly that corallina elongata is much more competitive than the majority of others adsorbents for the adsorption of MB from aqueous solutions.

Table-3: Sorption capacity of low cost sorbents for MB uptake.

Adsorbent	Q_{max}(mg.g^{-1})	Reference
Corallina elongata	**34.42**	**This study**
Microcrystalline cellulose	**4.95**	**[35]**
Shirasu balloon (SB)	**26.17**	**[36]**
Polydopamine-Modified-SB	**36.23**	**[36]**
Yellow passion fruit waste	**2.17**	**[11]**
Posidonia oceanic fibres	**5.56**	**[14]**
Invasive marine seaweed	**5.23**	**[37]**
Rice hull ash	**50.51**	**[38]**
Madhuca longifolia leaf	**5.21**	**[39]**
Neem leaf powder	**8.76**	**[13]**

Effect of temperature and Thermodynamic parameters

To determine the temperature effect on the adsorption amount of MB onto CE, and the thermodynamic parameters, we performed the adsorption isotherms at 3 different temperatures (30, 40 and 50 °C), solution pH (9), adsorbent dose (2 g.L^{-1}) and initial MB concentration (50 mg.L^{-1}). Fig. 10.a showed the decreasing of MB adsorption amount from 15.10 to 14 mg.g^{-1}, with increasing temperature from 30 ˚C to 50 ˚C, which indicates that the adsorption phenomena of MB onto CE is exothermic, Similar phenomena have been found for MB adsorption on maize silk powder [40].

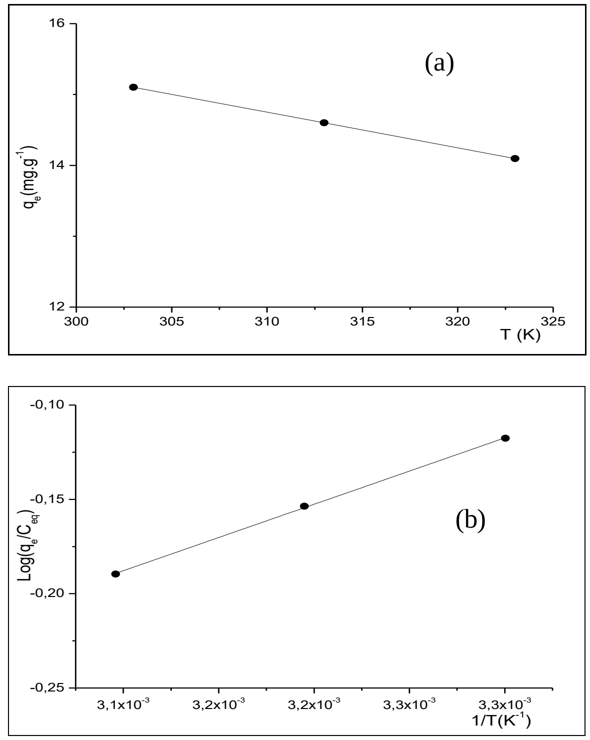


Fig. 10: Temperature effect on MB adsorption amount onto corallina elongate.

The thermodynamic parameters such as standard free enthalpy (ΔG), standard enthalpy (ΔH) and standard entropy (ΔS) were determined using the following equations:

$$\text{Log}\,(q_e / C_{eq}) = (\Delta S / 2.303\,R) - (\Delta H / 2.303\,RT) \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

where (q_e / C_{eq}) is called the affinity adsorption, The values of ΔH and ΔS were determined from the slope and the intercept of the linear plot of Log (q_e / C_{eq}) versus (1 / T) respectively, (Fig.10.b). These values were used to calculate ΔG [13].

Table-4 gives the values of the standard free enthalpy, the standard enthalpy and the standard entropy. The negative values of ΔG, ΔH and ΔS, indicate that the adsorption phenomenon is spontaneous, exothermic and the distribution order of molecules on the adsorbent increases with respect to that in the solution respectively, similar phenomena have been found for MB adsorption on maize silk powder [40]. A value of $\Delta H < 30$ kJ.mol^{-1} indicates that the adsorption of MB onto CE is a physical sorption [41, 42].

Table-4: Thermodynamic parameters of MB biosorption on corallina elongata.

T (K)	ΔG (kJ.mol^{-1})	ΔH (kJ.mol^{-1})	ΔS (kJ.mol^{-1}.K^{-1})
303	-6.7327		
313	-6.7324	-6.74	-0.024
323	-6.732		

Conclusion

In this study, we used the corallina elongata alga as novel and low-cost adsorbent material to remove methylene blue present in wastewater. The set of carried out characterization methods showed that the material consists essentially of calcium carbonate, which can be identified perfectly as a calcite containing magnesium, according to the results of the X-ray diffraction. This is confirmed by DTA and TGA, which demonstrated a behavior similar to that of thermal decomposition of calcium carbonate, also infrared spectroscopy corroborates these methods. Therefore, we can conclude that this material is a very good source of calcium carbonate.

Regarding its use as adsorbent, the first treatment has allowed to remove impurities and to increase the adsorption capacity. The kinetic experimental data were found to conform to the pseudo-second-order model with good correlation $R^2 = 0.99$ and equilibrium data were best fitted to the Langmuir model, with a maximum adsorption capacity of 34.4 mg.g^{-1}.

The thermodynamic study showed that the adsorption of methylene blue on Corallina elongata is a spontaneous and exothermic physisorption process. The adsorption results of methylene blue on CE, showed a good affinity between the two products with a high adsorption capacity.

Acknowledgments

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