



## Biosorptive uptake of methylene blue using Mediterranean green alga *Enteromorpha* spp.

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### ABSTRACT

Batch biosorption experiments were carried out for the removal of methylene blue, a basic dye, from aqueous solution using raw and dried *Enteromorpha* spp., Mediterranean green alga. A series of assays were undertaken to assess the effect of the system variables, i.e. contact time, solution pH and sorbent amount. The results had showed that sorption capacity was optimal using 6–10 solution pH range (i.e. maximum adsorption capacity of 274 mg/g). The minimum sorbent concentration experimentally found to be sufficient to reach the total removal of the dye molecules from the aqueous solution was 5 g/L. Besides, equilibrium data were fitted using five linearisable isotherm models. The related results showed that the experimental data were very well represented by the Langmuir model for the linear regression analysis and both the Langmuir and Redlich–Peterson isotherm models for the non-linear analysis. In both cases, such modelling behaviour confirms the monolayer coverage of methylene blue molecules onto energetically homogenous *Enteromorpha* surface. In addition, an exhaustive comparative study was done to situate this marine biomass among other proposed sorbents.

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## 1. Introduction

Several biological, physical and chemical methods have been used for the treatment of industrial textile wastewater including microbial biodegradation, membrane filtration, oxidation and ozonation [1]. However, many of these technologies are cost prohibitive, especially when applied for treating large waste streams.

Consequently, adsorption techniques seem to have the most potential for future use in industrial wastewater treatment [2,3] because of their proven efficiency in the removal of organic and mineral pollutants and for economic considerations [4–6].

The most widely used adsorbent for this purpose is activated carbon, but its overlying cost [7,8] has led to search for cheaper alternative materials such as orange and banana peels [9], papaya seeds [10], *Ulva lactuca* [11,12], jackfruit peel [13] and *Posidonia oceanica* fibres [14–16].

The main focus of this study was to evaluate the biosorption capacity of the highly available, low cost and renewable green alga, *Enteromorpha* spp. for the removal of methylene blue (MB) as a model compound for basic dyes. The effects of contact time, pH and biomass amount on the sorption behaviour were investigated. Moreover, several equilibrium models were tested after both linear and non-linear regression analysis in order to fit the experimental

data and to understand the possible physiochemical interactions involved in the sorption phenomenon between the algae surface and the dye molecules. Besides, a comparative study on the sorption performance of *Enteromorpha* and other sorbents was also carried out, along with a statistical analysis on the effect of linear and non-linear modelling on the error deviation estimation.

## 2. Materials and methods

### 2.1. *Enteromorpha* genus: chemical and biochemical composition

Many studies were carried out on *Enteromorpha* spp. for several kind of utilisation including biogas generation [17] and even human consumption [18]. Basically, the major constituents in *Enteromorpha* spp. cellular wall are carbohydrate (mainly hemicellulose), followed by proteins, lipids, minerals and ether extract [19]. The biochemical analysis results published by Aguilera-Morales et al. [20] showed that *Enteromorpha* spp. has 9–14% protein; 21% of total fatty acid; 2–3.6% ether extract and 32–36%. Further interesting results could be found in the previously mentioned references [17–20].

### 2.2. Algae and dye solution preparation

The marine fibrous biomass, *Enteromorpha* spp., was manually collected from Chott Meriem bay (Eastern coast of Tunisia). The fibres were separated, washed with generous amounts of distilled water to remove the surface-adhered particles and then dried in

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### Nomenclature

$A_{RP}$	Redlich–Peterson isotherm constant [(L/mg) $^\beta$ ]
$B$	variation of adsorption energy (kJ/mol)
$B_T$	(=RT/b) is related to the heat of adsorption (J/mol)
$C_0$	initial concentration of methylene blue in the solution (mg/L)
$C_e$	equilibrium concentration of methylene blue in the solution (mg/L)
$K_E$	Elovich isotherm constant (L/mg)
$K_F$	Freundlich isotherm constant [(mg/g)(L/mg) $^{(1-n/n)}$ ]
$K_L$	Langmuir isotherm constant (L/mg)
$K_{RP}$	Redlich–Peterson isotherm constant (L/g)
$K_T$	Temkin isotherm constant (L/mg)
$M$	mass of <i>Enteromorpha</i> spp. fibres (g)
$n$	Freundlich exponent related to adsorption intensity (dimensionless)
$Q$	amount of methylene blue adsorbed per unit of biomass at time $t$ (mg/g)
$Q^\circ$	Langmuir monolayer adsorption capacity (mg/g)
$Q_e$	experimental amount of methylene blue adsorbed per unit of biomass (mg/g)
$Q_E$	Elovich maximum adsorption capacity (mg/g)
$R$	universal gas constant (8.314 J/mol)
$R^2$	squared regression correlation coefficient
$t$	time (min)
$T$	absolute temperature (K)
$V$	solution volume (L)

### Greek letter

$\beta$	Redlich–Peterson exponent (dimensionless)
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an oven at 40 °C for 48 h to a constant weight. The average particle size is ranged between 1 and 2 mm. The dried biomass was stored in desiccators for further use.

Methylene blue has been used in this study as a model molecule for basic dyes and because of his extensive use in sorption studies, which would enhance the forthcoming comparative section. Stock solutions were prepared by dissolving accurately weighed samples of dye in distilled water to give a concentration of 1000 mg/L and diluting when necessary. Initial pH was adjusted by adding dilute solutions of HCl or NaOH.

### 2.3. Batch adsorption experiment

Adsorption experiments were carried out by shaking 0.05 g of *Enteromorpha* fibres with 50 mL of dye solution (i.e. 1 g/L) for the desired dye concentration and pH. The isotherm assays were carried out by varying the biomass concentration from 0.1 to 2 g/L for an initial dye solution of 100 mg/L. Studies were conducted at 30 ± 2 °C using a thermo-regulated water bath operating at 50 oscillations per minute. Methylene blue residual concentration was estimated using the spectrophotometric technique at the wavelength of 665 nm. The samples were taken from the shaker at predetermined time intervals for the sorption dynamic assay and at equilibrium time for isotherms. The dye solution was centrifuged at 5000 rpm for 2 min and then analyzed. To calculate the dye removal, biosorption capacity at equilibrium time ( $Q_e$ ) or biosorption removal efficiency, will be determined respectively according to the following equations:

$$Q_e = \left[ (C_0 - C_e) \times \frac{V}{M} \right] \text{ (mg/g)} \quad (1)$$

$$\text{sorption removal percent} = \frac{(C_0 - C_e) \times 100}{C_0} (\%) \quad (2)$$

## 3. Results and discussions

### 3.1. Effect of exposure time: sorption dynamic

The relationship between contact time and MB biosorption onto raw *Enteromorpha* spp. fibres at an initial dye concentration of 100 mg/L is presented in Fig. 1. Hence, the biosorption dynamic profile of the studied dye onto *Enteromorpha* biomass can be divided into three main regimes: (i) linear increase in adsorption with time within the first half hour, (ii) transition regime (almost an hour) where the rate of adsorption levels off and (iii) a plateau regime. The same dynamic trend was signalled by using *P. oceanica* fibres [14]. Besides, the results show that the equilibrium states were attained at almost 90 min under the used operating conditions with the possibility to reach half of the sorption capacity in 15 min. For the coming experiences, and to ensure equilibrium, the isotherms experiments were left for 3 h. A similar behaviour was also observed for MB adsorption onto giant duckweed [21] and macro fungi [22].

### 3.2. Effect of pH

The aqueous solution pH exerts profound influence on the sorption uptake of dyes presumably due to its impact on both the surface binding-sites of the biosorbent and the ionisation/aggregation process of the dye molecules. In the present biosorption system, the effect of pH was investigated for values between 2 and 10 and the result was presented in Fig. 2. As shown, the equilibrium sorption capacity was minimum at pH 2 (40.21 mg/g) and increased up to 6, then remained nearly constant (70.35 mg/g) over the initial pH ranges of 6–10.

Indeed, as a green alga, the cell wall matrix of *Enteromorpha* contains different functional groups such as carboxyl, hydroxyl, sulphate and other charged groups which are created by their complex polysaccharides, protein and lipid components. Thus, at lower pH, the surface charge may get positively charged (i.e. protonation of the cell wall), thus making ( $H^+$ ) ions compete effectively with dye cations toward active sorption sites causing a decrease in the amount of adsorbed dye. In that case (lower pH), the biomass still able to adsorb MB, which could be attributed to the hydrogen ions acting as a bridging ligand between the alga cell wall and the dye molecule. Thereafter, at higher pH the alga polymeric components may get negatively charged (possible deprotonation), which

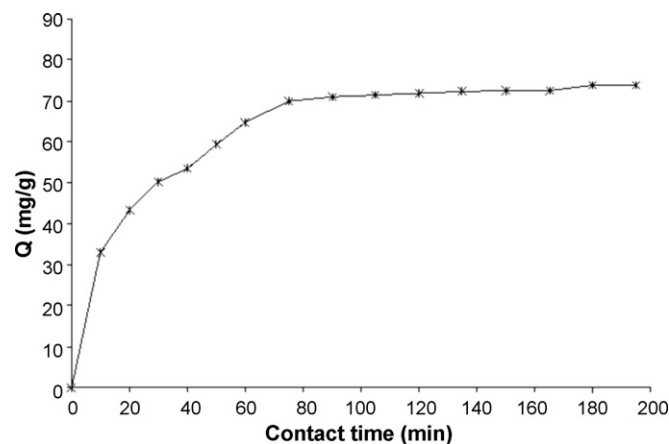


Fig. 1. Effect of contact time on biosorption amount of methylene blue onto *Enteromorpha* spp. (biomass concentration = 1 g/L, dye concentration = 100 mg/L, initial solution pH 6, temperature = 30 ± 2 °C).

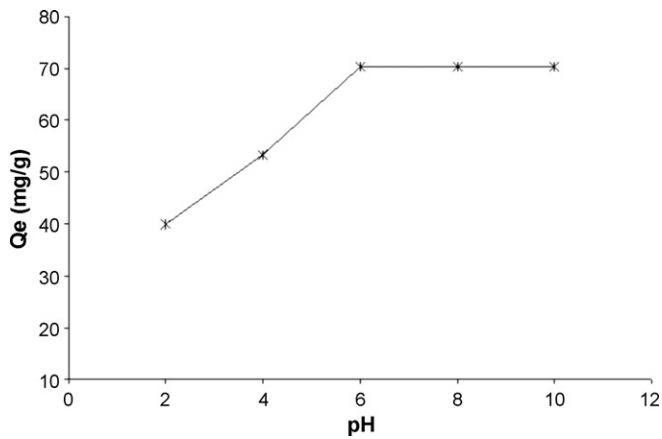


Fig. 2. Effect of pH on the biosorption capacity of methylene blue onto *Enteromorpha* spp. (biomass concentration = 1 g/L, dye concentration = 50 mg/L, temperature =  $30 \pm 2^\circ\text{C}$ ).

enhances the positively charged dye cations through electrostatic forces of attraction.

The same tendency was also recorded for MB uptake by *posidonia* fibres [14].

### 3.3. Influence of sorbent amount

The effect of biosorbent quantity on the removal of MB was investigated at 50 mg/L dye concentration. A range of 0.005–1 g of *Enteromorpha* fibres were mixed with 50 mL of the dye solution (i.e. 0.1–20 g/L). The result, displayed in Fig. 3, shows that an increase in the biomass quantity causes a decrease in the residual methylene blue concentration at equilibrium time and consequently an increase in the biosorption removal efficiency. Indeed, the biosorption removal efficiency values increased from 37% to 100%, as the biomass dose was increased from 0.1 to 5 g/L. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active adsorption sites. Quite similar tendency was reported for methylene blue adsorption onto Indian rosewood sawdust [23].

### 3.4. Adsorption isotherm modelling

#### 3.4.1. Mathematical background

Adsorption is usually modelled by isotherms which relate the relative concentrations of solute adsorbed to the solid ( $Q_e$ ) and in solution ( $C_e$ ). In the related literature, many models have been

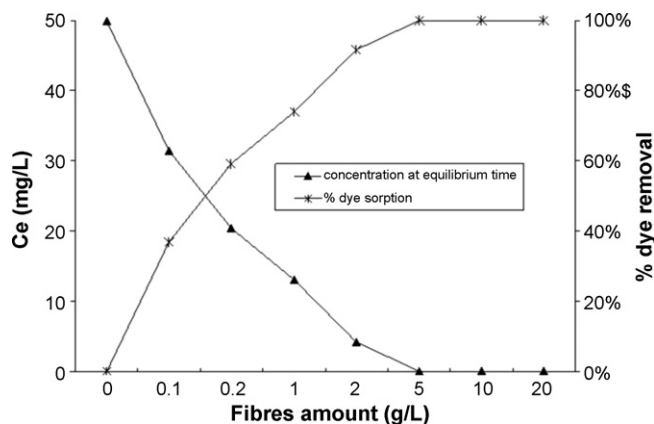


Fig. 3. Effect of algae amount on the removal of methylene blue (initial dye concentration = 50 mg/L, initial solution pH 6, temperature =  $30 \pm 2^\circ\text{C}$ ).

used to establish the most appropriate correlation for the equilibrium curves. In this study, the isotherms data were analyzed using five commonly used equilibrium models, Langmuir, Freundlich, Redlich–Peterson, Temkin and Elovich isotherm models. In this study, the theoretically predicted isotherm data were determined using the Microsoft Excel for linear analysis and SPSS 13.0 statistics software for non-linear assessment. Besides, and in order to optimize the non-linear iteration procedure, the runs were performed using three random initial values.

- (i) *The Langmuir model* [24] is valid for monolayer sorption onto a surface with a finite number of similar active sites. The well known expression of the Langmuir model is given by Eq. (3) and the derived linear forms in Eq. (4).

$$Q_e = \frac{Q^\circ K_L C_e}{1 + K_L C_e} \quad (3)$$

$$\frac{1}{Q_e} = \frac{1}{Q^\circ K_L} \frac{1}{C_e} + \frac{1}{Q^\circ} \quad (4)$$

- (ii) *The Freundlich model* [25] is an empirical equation based on sorption onto a heterogeneous surface is given below by Eq. (5) and its linear form by Eq (6):

$$Q_e = K_F (C_e)^{1/n} \quad (5)$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln(C_e) \quad (6)$$

- (iii) *The Redlich–Peterson model* [26] incorporates the features of the Freundlich and Langmuir isotherms into a single equation and presents a general isotherm equation as follows:

$$Q_e = \frac{A_{RP} C_e}{1 + K_{RP} C_e^\beta} \quad (7)$$

The linear form of the Redlich–Peterson (R–P) equation is given by Eq. (8):

$$\ln \left( \frac{A_{RP} C_e}{Q_e} - 1 \right) = \beta \ln(C_e) + \ln K_{RP} \quad (8)$$

The exponent,  $\beta$ , as it lies between 0 and 1, has two limiting behaviours: Langmuir form for  $\beta = 1$  and Henry's law form for  $\beta = 0$ .

- (iv) *The Temkin model* [27] deals with the heat of adsorption and the involved sorbent/sorbate interactions. Its main assumption is the uniformity in the distribution of binding energies up to some maximum binding energy. The equation of the Temkin model and its linear form are presented by Eqs. ((9) and (10)).

$$Q_e = \frac{RT}{b} \ln(K_T C_e) \quad (9)$$

$$Q_e = B_T \ln(K_T) + B_T \ln(C_e) \quad (10)$$

- (v) Basically, the *Elovich model* [28] is supported on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. Its equation and the related linear form are expressed by Eq. ((11) and (12)).

$$\frac{Q_e}{Q_E} = K_E C_e \exp \left( -\frac{Q_e}{Q_E} \right) \quad (11)$$

$$\ln \left( \frac{Q_e}{C_e} \right) = \ln(K_E Q_E) - \frac{Q_e}{Q_E} \quad (12)$$

#### 3.4.2. Linear regression analysis

The calculated isotherm constants evaluated from the linear plots at  $30^\circ\text{C}$  are given in Table 1. The fitting aptitude of the five isotherm models is depicted in Fig. 4. As shown, the best-fit equilibrium model was determined based on the linear squared

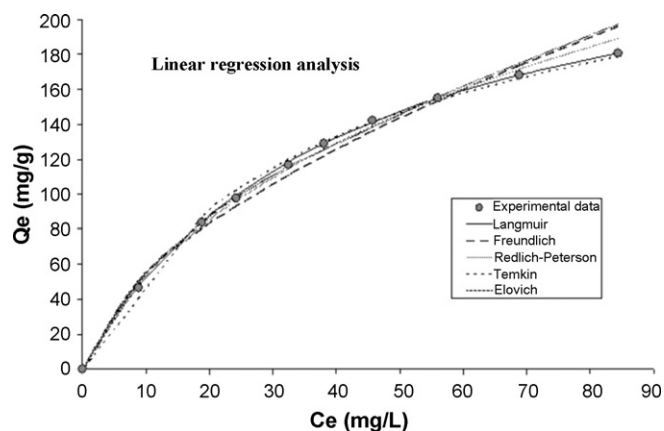
**Table 1**  
Isotherm modelling parameters related to the biosorption of MB onto raw *Enteromorpha* spp.: linear approach.

Langmuir isotherm	
$Q^{\circ}$ (mg/g)	270.27
$K_L$ (L/mg)	0.02
$R^2$	<b>0.999</b>
MPSED	<u>0.008</u>
ARED	<u>0.562</u>
Freundlich isotherm	
$K_F$ ( $\text{mg}^{1-1/n}\text{L}^{1/n}\text{g}^{-1}$ )	14.01
$n$	1.67
$R^2$	0.981
MPSED	0.063
ARED	4.989
Redlich–Peterson isotherm	
$A_{RP}$ (L/mg) $^{\beta}$	8.22
$K_{RP}$ (L/g)	0.10
$\beta_{RP}$	0.73
$R^2$	0.991
MPSED	0.030
ARED	2.194
Temkin isotherm	
$B_T$ (J/mol)	61.14
$K_T$ (L/mg)	0.22
$R^2$	0.993
MPSED	0.055
ARED	3.232
Elovich isotherm	
$Q_E$ (mg/g)	151.51
$K_E$ (L/mg)	0.05
$R^2$	0.980
MPSED	0.048
ARED	3.016

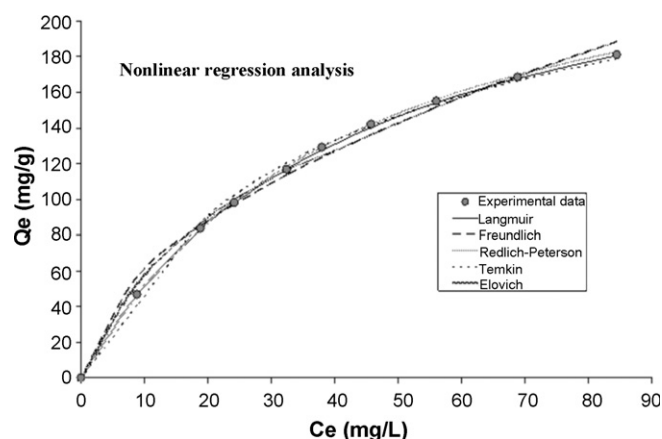
Highest  $R^2$  in bold and lowest MPSED and ARED underlined.

regression correlation coefficient ( $R^2$ ), the average relative error deviation (ARED) and the Marquardt's percent standard error deviation (MPSED). Further information on those error functions and the applicability of other statistical tools to predict best-fitting isotherm models could be found in Ncibi et al. [29].

From Table 1, it was observed that the equilibrium sorption data were very well represented by the Langmuir isotherm by providing the highest with correlation coefficient ( $R^2 = 0.999$ ) and the lowest ARED (0.562) and MPSED (0.008). Therefore, the main assumption that could be made is the monolayer coverage process of methylene blue molecules onto *Enteromorpha*'s sorptive sites. Furthermore, the value of Freundlich exponent ( $n = 1.67$ ) in the range of 1–10, indicates a favourable adsorption [30]. Also, the very high adsorp-



**Fig. 4.** Linear isotherm modelling fit related to the biosorption of MB onto raw *Enteromorpha* spp. at  $30 \pm 2^\circ\text{C}$ .



**Fig. 5.** Non-linear isotherm modelling fit related to the biosorption of MB onto raw *Enteromorpha* spp. at  $30 \pm 2^\circ\text{C}$ .

tion capacity (270 mg/g) indicates the strong electrostatic force of attraction between dye molecules and binding-sites on the surface of the algae [31].

### 3.4.3. Non-linear regression analysis

As non-linear equations, the linearization step of the isotherm models leads to the alteration of the error distribution after transforming the data to a linear form. Thus, in order to avoid such problem, a non-linear regressions analysis was performed for each one of the five models. Fig. 5 shows the experimental equilibrium data and the predicted theoretical isotherms for the sorption of MB onto *Enteromorpha* surface. The calculated isotherm constants by non-linear method were shown in Table 2.

**Table 2**  
Isotherm modelling parameters related to the biosorption of MB onto raw *Enteromorpha* spp.: non-linear approach.

Langmuir isotherm	
$Q^{\circ}$ (mg/g)	273.79
$K_L$ (L/mg)	0.02
$R^2$	<b>1.000</b>
MSPED	<u>0.009</u>
ARED	<u>0.658</u>
Freundlich isotherm	
$K_F$ ( $\text{mg}^{1-1/n}\text{L}^{1/n}\text{g}^{-1}$ )	18.09
$n$	1.89
$R^2$	0.983
MPSED	0.090
ARED	4.699
Redlich–Peterson isotherm	
$A_{RP}$ (L/mg) $^{\beta}$	6.37
$K_{RP}$ (L/g)	0.02
$\beta_{RP}$	1.00
$R^2$	<b>1.000</b>
MPSED	<u>0.009</u>
ARED	<u>0.575</u>
Temkin isotherm	
$B_T$ (J/mol)	61.14
$K_T$ (L/mg)	0.22
$R^2$	0.994
MPSED	0.055
ARED	3.232
Elovich isotherm	
$Q_E$ (mg/g)	135.16
$K_E$ (L/mg)	0.06
$R^2$	0.988
MPSED	0.060
ARED	3.751

Highest  $R^2$  in bold and lowest MPSED and ARED underlined.

**Table 3**Comparison of the adsorption capacities of *Enteromorpha* spp. and other adsorbents for methylene blue uptake from aqueous solutions.

Adsorbents	Temperature (°C)	Equilibrium time (h)	pH	Q° (mg/g)	References
<i>Enteromorpha</i> spp.	30	3	6	273.73	This study
Pomelo peel	30	5.15	7	344.83	[32]
<i>Phellinus igniarius</i>	20	48	7.5	204.38	[22]
Jalshakti polymer	25	2	5.5	172.4	[33]
Mango seed kernel	25	48	8	153.84	[34]
Giant duckweed	25	24	7	119.05	[21]
Sewage sludge	25	3	–	114.94	[35]
Cedar sawdust	20	5	7	110.97	[36]
Nuchar C-190 AC	25	2	6	104.2	[33]
Treated <i>Parthenium</i> weed	26	2	7.2	88.49	[37]
Crushed brick	20	5	7	80.6	[36]
Coconut bunch waste	30	5.15	7	70.92	[38]
Clay	20	2	5.65	58.20	[39]
Rice husk	32	48	8	40.59	[40]
Banana peel	30	24	6–7	15.9	[9]
Coconut coir dust AC	25	2	8	14.36	[41]
Orange peel	30	24	>7	13.9	[9]
<i>Ulva lactuca</i>	25	2	10	10.99	[12]
Coir pith AC	25	1.5	6.9	5.87	[42]
Fly ash	30	2	8	5.57	[43]
<i>Posidonia oceanica</i>	30	3	6	5.56	[14]
Guava seeds AC	30	0.75	7	0.66	[44]

AC: activated carbon.

From Table 2, the models showing the best fit to the equilibrium sorption data are Langmuir and Redlich–Peterson isotherms. Therefore, in addition to the Langmuir isotherm (already pointed out by the linear analysis), the sorption process can also be represented by the Redlich–Peterson model. Indeed, with a value of  $\beta_{RP}$  equal to unity, the Redlich–Peterson equation is transformed into the Langmuir expression. Such behaviour was due to precise estimation of the  $\beta_{RP}$  constant. The value of this constant was poorly estimated via linear analysis due to the linearization process. Furthermore, the error provoked by the transformation of a non-linear expression to a linear one seems to have a relation with the number of parameters in the model. Indeed, comparing the constants of the Redlich–Peterson model (i.e. three parameters equation) with those of the other models (i.e. two parameters equations); the impact of the distortion made by the linearization is more obvious for the case of the R–P isotherm. For instance, the  $\beta_{RP}$  value calculated from the linear analysis (0.73) is significantly different from the one deduced after a non-linear regression analysis (1.00). Such difference in the estimation of this sole parameter would lead to erroneous assumptions. Furthermore, the error deviations calculated for the case of the R–P model clearly shows the misleading results obtained with the linear analysis for non-linear equations for three parameters models. Indeed, by comparing the results in Tables 1 and 2, the  $R^2$  value increased from 0.991 (linear) to the unity (non-linear). Besides, the ARED and MPSED both decreased respectively from 2.194 (linear) to 0.575 (non-linear) and from 0.030 (linear) to 0.009 (non-linear).

On the other hand, according to the modelling results of the equilibrium data related to the present sorption system, it is interesting to mention that, contrary to the three-parameter equation (R–P model), all other two-parameter models seem not to be affected by whether the analysis is carried out linearly or non-linearly. Indeed, for the Langmuir, Freundlich and Elovich models, the deduced constants slightly differ with respect to the regression analysis approach. The same behaviour is very clear for the case of the two-parameter Temkin equation where both the constants and the calculate error deviation are similar.

Thus, based of the presented results of both linear and non-linear modelling, we recommend the use of the non-linear regression analysis to model experimental equilibrium data and, therefore, have a solid background to use the assumptions related to the best-

fitting model(s) which is quite important for design purposes. Such recommendation is logical (i.e. non-linear analysis for non-linear equation). But, as for the present study, the use of linear regression analysis, which is very commonly used in adsorption-related articles, is also possible provided that all the tested models have the same number of inner parameters. Otherwise, the iteration and error procedure used to estimate the constants in three-parameter equations in the linear approach would lead to wrongly estimated constants.

### 3.5. Comparing the sorption capacity of *Enteromorpha* spp. with other sorbents

Moreover, in order to situate the *Enteromorpha* biomass and its very high sorption capacity biosorbent among those used to remove MB from aqueous solutions (i.e. natural resources, georesources, wastes, carbonaceous materials, polymers, etc.), an exhaustive comparison based on the commonly calculated Langmuir's saturation capacity  $Q^\circ$  was made. The results, illustrated in Table 3, had shown that with a sorption capacity of about 273 mg/g, the *Enteromorpha* fibres are a very performing and promising biomaterial to remove basic dyes even when compared other sorbents well known form their high adsorption capabilities, activated carbons. For instance, *Enteromorpha* biomass is able to adsorb nearly three times more than a commercial activated carbon (104 mg/g) [32]. Furthermore, compared to other marine bioresources, the *Enteromorpha* fibres seem to be a very performing biosorbent. Actually, our team previously worked on another marine biomass, *P. oceanica* fibres [14], for which the maximum adsorption capacity was 5.56 mg/g. Then, using the *Enteromorpha*, the sorption capacity was considerably enhanced to reach 273 mg/g (i.e. 45 times more) under the same operating conditions (contact time 3 h, temperature 30 °C and pH 6).

Thus, low cost, available and renewable *Enteromorpha* spp. fibres seem to be very competitive to other dye-sorbent materials and, therefore, using this biomass to remove other kind of pollutants is quite interesting for further studies. Chemical activation of raw *Enteromorpha* fibres could also be an interesting subject of study to improve the sorption capacity by tailoring the surface chemistry to absorb a specific type of pollutant from aqueous media. Studies on both research themes are in progress.



#### 4. Conclusion

In the present research, methylene blue removal from aqueous solution through biosorption onto raw *Enteromorpha* spp. fibres was investigated. The biosorption capacity was estimated as a function of contact time, initial pH and biosorbent dosage. The results showed that the biosorption capacity was optimal under alkaline conditions (pH 6–10). The minimum amount of biomass needed to fully remove MB molecules from aqueous solution was 5 g/L. The equilibrium sorption phenomena were found to be well described by Langmuir isotherm for linear regression analysis and both Langmuir and Redlich–Peterson models when non-linear analysis was carried out. The comparison of the biosorption aptitude between *Enteromorpha* fibres and other adsorbent materials indicated that the experimented Mediterranean algae, showed a very good biosorption capacity toward the tested basic dye.

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