BIOSORPTION OF METHYLENE BLUE ON CHEMICALLY MODIFIED CHAETOPHORA ELEGANS ALGA BY HCl AND CITRIC ACID

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ABSTRACT

Chemical modification of Chaetophora Elegans algae with HCl and citric acid was undertaken in order to improve the methylene blue adsorption. The modified algae with 1 M HCl showed an increase in the maximum uptake from 143 mg g\(^{-1}\) to 320 mg g\(^{-1}\) due to elimination of carbonate. The modified algae with 1M citric acid showed an important decrease in the uptake from 143 mg g\(^{-1}\) to 20 mg g\(^{-1}\) due to increase in the cross linking degree. Acid concentration used in the chemical modification (0.1 M -1 M) is the major parameter affecting the maximum uptake. The temperature of the chemical modification has a small effect on the uptake. Langmuir-Freundlich isotherm model fitted better the isotherm adsorption data for all samples studied. Pseudo second order model was well in line with the experimental data. The adsorption rate constant \((K_2)\) is higher for modified algae with HCl than that of raw algae. The activation thermodynamic parameters \(E_a\), \(\Delta H^\#\), \(\Delta S^\#\) and \(\Delta G^\#\) were calculated. The maximum uptake is independent of isotherm adsorption temperature in the range studied.

Keywords: Modified algae, citric acid, HCl, methylene blue, isotherm adsorption, kinetic.

INTRODUCTION

The extensive use of dyes poses pollution problems. They reduce light penetration and photosynthesis; in addition, some dyes are carcinogenic [1]. Several methods exist for reducing the color in textile effluent streams: adsorption, oxidation-ozonation, biological treatment, coagulation-flocculation and membrane processes. The adsorption process is one of the most effective and attractive processes for wastewaters treatment. The most commonly used adsorption agent in industry is activated carbon, which has also been extensively studied for the removal of dyes [2-6]. However; the high operation costs of regeneration prevent the large-scale application of activated carbon. Therefore, a number of other non-conventional adsorbents have been evaluated for the treatment of wastewaters. Natural materials, biosorbents [7-10], and waste materials from industry and agriculture represent potentially more economical alternative adsorbents [11-16].

Generally, the sorption capacity of a crude biosorbent is low, but chemical modification can improve the sorption capacity of these biomaterials. The chemical treatment increases the number of the active sites or replaces the existing sites by more attractive ones. Many chemical reagents, organic or inorganic are used for this purpose (Table 1). The reagents used for this purpose are citric acid [17 – 22], HCl [23- 26], CaCl\(_2\) [25, 27], formaldehyde [25, 28], methanol [24, 27, 29], KMnO\(_4\) [30], oxalic acid [31] and NaOH [32]. Citric acid is the mostly reagent used since it introduces carboxylate group at the surface of the biomass, whereas HCl breaks the pectose down to pectin or pectic acid. And also proteins located in cell wall are denaturated by treatment and structural changes occurred [23].

Rubin et al. noted that the adsorption capacity of the Sargassum muticum biomass improved after modification with CHCl\(_3\) / CH\(_3\)OH [24]. The pretreatment of
Penicillium chrysogenum with polyethylenimine using glutaraldehyde increased significantly the adsorption capacities of the biomass toward metal ions [33]. Bätzias and Sidiras treated beech sawdust using CaCl$_2$ and they found that the adsorption capacity of the adsorbent towards dye compounds was greatly increased after the chemical modification [34].

In the environmental field, methylene blue is frequently used as a model of organic cation in the search of new adsorbent biomass based materials, which can be used as an alternative for activated carbon [35]. This work deals with the adsorption of methylene blue by chemically modified biomass of the Chaetophora algae by HCl and citric acid (with 3- COOH).

**EXPERIMENTAL**

Chemical modification of algae was studied in order to improve the adsorption uptake of raw algae. Several operating conditions affecting the dye uptake were studied in order to optimize the overall adsorption process. Thus the experiments were carried out with different chemical reagents, different reagent concentration, and temperature of the chemical reaction. The reagents used for this purpose were citric acid and HCl. The concentrations of the acid were 0.1, 0.5 and 1 M. The chemical reaction between the acid and the raw algae (RG) in the water bath was occurred at 25, 40, 50 and 60°C. The general procedure applied for this purpose was according to that mentioned in ref. 19.

**Dye solution preparation**

The dye used in this study is methylene blue (C.I. 52015, BDH, 82 %), a cationic thiazine dye. Stock solutions of methylene blue, were prepared without further purification, by dissolving accurately weighed dye in distilled water at a concentration of 500 mg dm$^{-3}$. Eight working solutions (62.5, 125, 250, 300, 350, 400, 450, 500 mg dm$^{-3}$) were prepared in order to draw the adsorption isotherm and calculate its parameters.

**Surface modification**

Chaetophora elegans algae (collected in June 2010, and prepared as described in a previous work was mixed with various concentrations of acid (HCl or Citric acid) [36]. 5.0 g biomass to 50 mL of a selected acid concentration (0.1, 0.5 and 1M) and stirred for 4 h at a selected water bath temperature (25, 40, 50, 60°C). The acid/biomass was then heated at 110°C for 4 h, afterward; the dried powder was washed and filtered several times with distilled water (~ 500 ml) until the pH of water became neutral and the drain water became clear. The washed biomass was finally dried in an oven at 110°C for 16 h. and preserved for future use. The biomass weight loss was determined after each treatment. For simplicity the samples treated with citric acid are called x Cit y, where x and y represent the concentration of the acid used and y the temperature of the first step in the chemical reaction. Three samples of raw algae was treated in the same manner at 40, 50 and 60°C by replacing the acid solution with distilled water in order to use them as references.

**Batch mode adsorption studies**

Batch adsorption experiments were conducted to evaluate the MB adsorption capacities of the raw and modified biomasses. The different parameters affecting the adsorption such as pH, mass of algae, equilibrium time, …) are already determined in a previous work [37].

0.1 g of modified biomass was added to 100 ml plastic erhnmeyer, containing 50 mL of MB solutions of different concentration and agitation in the water bath shaker at 200 rpm at 25±1°C for 3h 30 min, which was sufficient to attain equilibrium. Eight concentrations of MB ranging from 60 to 500 mg/L were used in order to draw the adsorption isotherm and deduce $q_{\text{max}}$. After equilibrium being attained, the samples were centrifuged and the remaining concentration in the supernatant solution were analyzed at 666 nm, $\lambda_{\text{max}}$ of MB, using a double beam UV – Visible spectrophotometer (Specord 200, Analytical Jena), after appropriate dilution with distilled water. Isotherm experiments were carried out in duplicate. For the kinetic study, several samples are prepared in the same conditions (0.1 g of biomass, 50 mL of MB of fixed concentration). Then 2 ml is withdrawn at a selected time in order to determine the adsorption rate constant and the order of adsorption.

The amount of dye adsorbed per unit weight of alga at equilibrium; $q_e$ (mg g$^{-1}$) or at time $t$; $q_t$ (mg g$^{-1}$) were calculated according to the following relations

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad (1)$$

$$q_t = (C_o - C_t) \times \frac{V}{m} \quad (2)$$
The initial and equilibrium concentrations of dye (mg dm$^{-3}$), respectively. $V$ is the volume of the dye solution (L) and $m$ is the amount of the adsorbent used (g). To determine the percentage of dye removal equation (3) is used:

$$\% \text{ removed} = \left( \frac{C_o - C_e}{C_o} \right) \times 100 \quad (3)$$

**Characterization of the modified algalae**

The raw and the modified algalae were analyzed and characterized by FTIR (spectrophotometer Thermo, Nicolet IR 200, dilution with KBr) to know the functional groups that might intervene in the adsorption process. XR diffraction is carried out with D8 Focus Bruker (Cu $K_{\alpha}$ 1.54 Å at 50 KV) to observe any change in the modified biomass with respect to raw algalae.

**RESULTS AND DISCUSSION**

**FTIR and XR diffraction analysis**

The infrared spectrum of raw algalae (RG), shown in Fig. 1, displays a number of absorption peaks, indicating its complex nature. Several bands were found at 3350 cm$^{-1}$ (-OH or –NH$\_2$), 2915 cm$^{-1}$ (-CH or COOH), 1620 cm$^{-1}$ (>C=O), and 1060 cm$^{-1}$ (C-O or >S=O).

Effervescence is observed immediately after addition of HCl and citric acid to raw algalae, but it is stronger with HCl. Chemical reaction occurred between the acid and the carbonate already presents in the protective wall of algalae, leading to the formation of CO$_2$ and a dramatic decrease in algalae weight. The weight loss is more affected by the concentration and the nature of the acid used rather than by the temperature of the chemical treatment: ~ 20 % with 0.1 M HCl, ~ 40 % with 0.5 M HCl and ~ 70 % with 1 M HCl. Similar decreases in the amount of biomass were found after HCl wash and formaldehyde cross-linking by Lodeiro et al. [38]. The authors explained the decrease by the replacement of Ca$^{2+}$, and Mg$^{2+}$ bound to active sites in the raw biomass by H$^+$. The FTIR spectrum of HCl modified algalae is similar to that of raw algalae with few differences: decrease in the strong peak at 1430 cm$^{-1}$ and in the medium peak at 866 cm$^{-1}$ (Fig. 1). These two peaks are characteristic bands of carbonate. The decrease in the peak’s heights and in the weight of algalae remained after chemical treatment is proportional to HCl concentration used. So the chemical modification with HCl decreases the amount of carbonate in the raw biomass and let the algalae more pure. Thermal analysis (TG-DSC) on Carolina algalae showed a sharp decrease at 786°C (endothermic) attributed to the conversion of CaCO$_3$ to CaO (s) and CO$_2$ (g) [28].

The crystalline state of raw algalae is good as shown by its XR diffraction spectrum. The XR diffraction spectra of algalae before and after treatment with HCl are completely different (Fig. 2). Three peaks at 20: 14.64, 17.1, and 22.92 became more intense after chemical treatment with HCl, but the intense peak in RG and in CaCO$_3$ (20: 29.54, 100 %) decreased. We attributed the
decrease of this peak in HCl 40 to decrease in CaCO₃ amount. According to XR diffraction, the chemical modification with HCl affects strongly the chemical composition of algae.

After chemical modification with 1 M citric acid, the broad band of OH at 3365 cm⁻¹ is divided into several bands (OH of COOH and OH of alcohol). The intensity of the band at 2914 cm⁻¹ which corresponds to C-H increases dramatically. New bands appeared after reaction with citric acid at 1615 and 1336 cm⁻¹, which can be assigned to C=O stretching, indicating the introduction of a new COOH sites (Fig. 3) [19]. The same behavior

![Fig. 3. FTIR spectra of raw algae and modified algae with 1 M citric acid treated at 62°C.](image)

![Fig. 4. XR diffraction spectra of raw algae and modified algae with 1 M citric acid treated at 62°C.](image)

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Pollutant</th>
<th>Treatment</th>
<th>Q_max (mg g⁻¹)</th>
<th>Sources</th>
</tr>
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<tbody>
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<td>Sargassum muticum</td>
<td>MB</td>
<td>HNO₃</td>
<td>279 ± 4</td>
<td>Pilar et al. [17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHCl₃/MeOH</td>
<td>841 ± 81</td>
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<tr>
<td></td>
<td></td>
<td>Me₂CO reflux</td>
<td>860±100</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Me₆CO</td>
<td>402 ± 8</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>MeOH</td>
<td>416 ± 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃OH/H₂O</td>
<td>358 ± 8</td>
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<td>Sargassum Muticum</td>
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<td>237</td>
<td>Vincente et al. [24]</td>
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<tr>
<td></td>
<td></td>
<td>HCl</td>
<td>279</td>
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<tr>
<td>Corynebacterium Glutamicum</td>
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<td>Citric acid</td>
<td>25±0.9</td>
<td>Y.-S.Yun et al. [19]</td>
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<tr>
<td>Carolina</td>
<td>MB</td>
<td>H₂CO</td>
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<td>Hammud et al. [28]</td>
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<tr>
<td>Chaetophora Elegans</td>
<td>MB</td>
<td>HCl</td>
<td>143</td>
<td>This work</td>
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<td></td>
<td>20</td>
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</tr>
<tr>
<td>Rice Straw</td>
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<td>Gong et al. [18]</td>
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<td>Pinus Merkusii (wood)</td>
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<td>Citric acid</td>
<td>7.71</td>
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<td></td>
<td>Cu(II)</td>
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<td>2.56</td>
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<td>82.64</td>
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<td></td>
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<td>23.70</td>
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<td></td>
<td></td>
<td></td>
<td>22.5</td>
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</tr>
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</table>

Table 1. Comparison of the uptake of pollutants by modified and unmodified algae.
is observed with the other treated samples (0.1 M and 0.5 M), but it is more pronounced with 1 M of citric acid or 1 M of HCl.

The XR diffraction spectra of algae before and after treatment with citric acid are also very different (Fig. 4). For example, the sample 1Cit 62 showed the appearance of new intense peaks ($2\theta$: 16.48, 21.16, 31.36) and the disappearance of that at 29.54 (100 % in the raw algae). We thought that an important chemical reaction occurred between the raw algae and the acid added. The chemical modification occurred with HCl is different from that occurred with citric acid.

The weight loss of samples treated with 0.1 M, 0.5 M citric acid is the 8 %, and 2 %. It’s much lower than that obtained with HCl due to introduction of citric acid to wall cells.

**Isotherm modeling analysis**

Several isotherm models are used in the literature to find the relationship between $q_e$ and $C_e$. The experimental data related to the adsorption of MB molecules onto the algal biomass at different temperatures were fitted using Langmuir [39], Freundlich [40], Temkin [41], and combined Langmuir-Freundlich equations [42]. In this study, the theoretically predicted isotherm data were determined using a non-linear regression analysis via the Origin 7 software (in order to avoid the error induced using the linearized forms).

(i) **The Langmuir model**: The Langmuir isotherm suggests that MB adsorption is limited with monolayer coverage and there is no significant interaction among adsorbed species.

$$q_e = \frac{q_{max} \times b \times C_e}{1 + b \times C_e} \quad \text{with} \quad b = \frac{K_{ads}}{K_{des}} \quad (4)$$

with $q_{max}$ (mg g$^{-1}$) is the maximum sorbate uptake under the given conditions and $b$ (dm$^3$ mg$^{-1}$) is the adsorption equilibrium constant, related to the affinity between the adsorbent and sorbate.

(ii) **The Freundlich model**: The Freundlich relationship is an exponential one expressed as follows:

$$q_e = k \times C_e^n \quad (5)$$

where $k$ is the Freundlich constant. The Freundlich isotherm exponent $n$ is considered as a heterogeneity factor.

(iii) **Temkin isotherm**: The Temkin isotherm deals with the heat of adsorption and the involved sorbent/sorbate interactions.

$$q_e = \frac{RT}{b} \left( \ln K_f + \ln C_e \right) = A + B \times \ln C_e \quad (6)$$

where $B$ is a factor related to the heat of adsorption and $K_f$ is Temkin equilibrium constant (dm$^3$ mg$^{-1}$).

(iv) **Combined Langmuir-Freundlich**: Basically, it is an equation combining the previously mentioned Langmuir and Freundlich isotherms

$$q_e = \frac{q_{max} \times b \times C_e^n}{1 + b \times C_e^n} \quad (7)$$

**Modified algae with HCl**

The experimental isotherm adsorption data of raw algae fitted better Langmuir-Freundlich isotherm than Langmuir model (See Table 2). The untreated raw algae (collected two years ago) and the treated with distilled water at 40, 50 and 62°C showed an average of $q_{max}$ equal to 143 $\pm$ 5 mg g$^{-1}$. The raw biomass (organic compound) looses its adsorption property with storage time. In a previous work, the maximum uptake of MB onto fresh collected algae was much higher (300 mg g$^{-1}$) [37]. The decrease in $q_{max}$ is related to deterioration of the external surface.

The HCl modified algae showed an increase in the $q_{max}$ (Fig. 5 and 6). The increase in the maximum uptake is more related to HCl concentration than to the reaction temperature (Fig. 6, Table 2). According to $R^2$ values and $q_{max}$, Langmuir-Freundlich model is more realistic than Langmuir model (Table 2). The maximum uptake passed from 143 mg g$^{-1}$ (for RG) to 320 mg g$^{-1}$ for 1 HCl 25. The difference in the uptake is manifested for high initial MB concentration ([MB]$o$ > 150 mg dm$^{-3}$). The remained concentration of MB in contact with 500 mg dm$^{-3}$ of MB is 15.5 mg dm$^{-3}$ for 1HCl 40 against 144.4 mg dm$^{-3}$ for RG.

**Modified algae with citric acid**

Concerning, the isotherm adsorption of modified algae with citric acid, Langmuir - Freundlich model remained the best model in line with the experimental data, but all the samples showed a decrease in the uptake (Table 3, Fig. 5). The lowest $q_{max}$ is obtained with 1 M of citric acid (1Cit 62). The chemical modification with citric acid has a negative effect on the MB uptake. The concentration of citric acid is the important factor which
governs the decrease in the uptake. The \( q_{\text{max}} \) of 0.1Cit 25 (134 mg g\(^{-1}\)) is near to \( q_{\text{max}} \) of RG (143 mg g\(^{-1}\)) but that of 1Cit 25 is much lower (47 mg g\(^{-1}\)) (Table 3). The decrease in \( q_{\text{max}} \) may be due to increase in the cross-linking degree which would hamper the adsorption of MB or to denaturation of some active sites.

**Kinetic modeling analysis**

In the present study, non-linear regression method has been used to predict the best sorption kinetic model and also to obtain reliable kinetic parameters.

Lagergren first order kinetic expression was used mostly in the literature to show adsorption capacity on

![Fig. 5. Isotherm adsorptions of MB (at 25 °C) for modified algae with 1M HCl and 1M citric acid.](image)

![Fig. 6. Effect of HCl concentration and temperature, used in the chemical modification of algae on the maximum uptake according to non linear Langmuir- Freundlich model.](image)

<table>
<thead>
<tr>
<th>Models</th>
<th>( Q_{\text{max}} ) (mg g(^{-1}))</th>
<th>( b )</th>
<th>( K )</th>
<th>( n )</th>
<th>( A )</th>
<th>( B )</th>
<th>( n )</th>
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</thead>
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<td>Langmuir</td>
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<td>0.64</td>
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<td>0.77</td>
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<td>0.11</td>
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<td>73</td>
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<td>Temkin</td>
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<td>0.44</td>
<td>21.86</td>
<td>0.96</td>
<td>-25</td>
<td>91.42</td>
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<td>26.8</td>
<td>0.81</td>
<td>-13.22</td>
<td>84.9</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>( 0.967 )</td>
<td>( 0.99 )</td>
<td>( 0.946 )</td>
<td>( 0.99 )</td>
<td>( 0.98 )</td>
<td>( 0.988 )</td>
<td>( 0.995 )</td>
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<tr>
<td>Lang- Freund.</td>
<td>( 0.992 )</td>
<td>( 0.994 )</td>
<td>( 0.96 )</td>
<td>( 0.995 )</td>
<td>( 0.992 )</td>
<td>( 0.994 )</td>
<td>( 0.96 )</td>
</tr>
</tbody>
</table>

Table 2. Isotherm modeling parameters at 25 °C related to the biosorption of MB onto modified Chaetophora elegans with 1 M HCl treated at several temperatures (non-linear approach).
different adsorbents [43]. Pseudo-first first order equations are:

Non Linear form:

\[ q_t = q_e (1 - e^{-kt}) \]  \hspace{1cm} (8)

The pseudo-second order model is based on the assumption that the adsorption follows second order chemisorption [44]. The pseudo-second order model can be expressed as:

\[ q_t = \frac{q_e^2 \times K_2 \times t}{1 + K_2 \times q_e \times t} \]  \hspace{1cm} (9)

were \( t \) is the contact time (min), \( q_e \) (mg g\(^{-1}\)) and \( q_t \) (mg g\(^{-1}\)) are the amount of dye adsorbed at equilibrium and at any time. \( K_1 \) and \( K_2 \) are the first and the second rate adsorption constant respectively. For low initial MB concentrations (62.5 mg dm\(^{-3}\) - 150 mg dm\(^{-3}\)), the uptake of modified algae with HCl and the raw algae as a function of time is quit similar (Table 4). The adsorption rate of both kinds of algae is very fast in the first five minutes, then decreases to become negligible after 30 minutes (Fig. 7).

The dynamic sorption behavior of MB onto Chaetophora elegans’ surface under several initial dye concentrations was monitored and modeled. The related kinetic parameters and error derivation values are presented in Table 4. The first and the second adsorption models can be used to interpret the results, but according to \( R^2 \) values, the pseudo-second order model fit better the kinetic data.

**Effect of Temperature**

The activation parameters associated with the adsorption of 62.5 mg dm\(^{-3}\) MB onto RG and 1HCl40 are calculated as follow: plot of ln \( K_2 \) vs. 1/T gives the value of the activation energy (\( E_a \)), according to Arrhenius equation:

\[ \ln K_2 = -\frac{E_a}{R} T + cte \]  \hspace{1cm} (10)

The \( \Delta H^\neq \) and \( \Delta S^\neq \) value can be calculated from Eyring plot:

\[ \ln \left( \frac{K_2}{T} \right) = \ln \left( \frac{k_B}{h} \right) + \frac{\Delta S^e}{R} - \frac{\Delta H^e}{RT} \]  \hspace{1cm} (11)

where \( k_B \) = Boltzmann’s constant (1.381x10\(^{-23}\) J·K\(^{-1}\)), \( h \) = Plank’s constant (6.626x10\(^{-34}\) J·s) and \( \ln (k_B/h) = 23.76 \)

The free activation enthalpy \( \Delta G^\neq \) is equal to:

\[ \Delta G^\neq = \Delta H^\neq - T \times \Delta S^\neq \]  \hspace{1cm} (12)

The linear equation of ln \((K_2)\) vs. \(10^3/T\) is \( -5.03 +15.05 \)

for modified algae with 1 M HCl (Fig. 8). The activation energy and the others kinetics parameters in the range of temperature studied (23 °C - 32 °C) are listed in Table 5.

**Table 3.** Isotherm modeling parameters at 24ºC related to the biosorption of MB onto modified Chaetophora elegans algae with citric acid treated at 25°C and 60°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir</th>
<th>Langmuir - Freundilch</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( R^2 )</td>
<td>( q_{max} )</td>
</tr>
<tr>
<td>RG</td>
<td>0.93</td>
<td>160</td>
</tr>
<tr>
<td>0.1Cit 25</td>
<td>0.957</td>
<td>166.7</td>
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<tr>
<td>0.1Cit 60</td>
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<td>0.5Cit 25</td>
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<td>0.5Cit 60</td>
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</tr>
<tr>
<td>1Cit 25</td>
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<td>42</td>
</tr>
<tr>
<td>1Cit 60</td>
<td>0.95</td>
<td>19.4</td>
</tr>
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</table>
The chemical modification by HCl did not affect strongly the activation thermodynamic parameters.

CONCLUSIONS

Chemical modification of Chaetophora Elegans algae with HCl and citric acid has opposite action with respect to the MB uptake. The modified algae with HCl showed an increase in the maximum uptake, proportional to HCl concentration used due to elimination of carbonate. Modified algae with 1 M HCl gave the best uptake \( (q_{\text{max}} \text{ increased from 143 mg g}^{-1} \text{ to 320 mg g}^{-1}) \). The modified algae with citric acid showed an important decrease in the uptake due to increase in the cross linking degree. The decrease in \( q_{\text{max}} \) is inversely proportional to citric acid concentration used (0.1 M - 1 M). Modified algae with 1 M citric acid gave the worst uptake \( (q_{\text{max}} \text{ decreased from 143 mg g}^{-1} \text{ to 20 mg g}^{-1}) \). Acid concentration used in the chemical modification is the major parameter affecting the maximum uptake. The temperature of the chemical modification has a small effect on the uptake (25°C-60°C). Langmuir-Freundlich isotherm model fitted better the isotherm adsorption data for all samples studied. Pseudo-first and pseudo-second order kinetic models were applied to the adsorption dynamic data. Pseudo second order model was well in line with the experimental data. The adsorption rate constant \( (K_2) \) is higher for modified algae with HCl than that of raw algae.

Table 4. Pseudo first and pseudo second order adsorption kinetic parameters at 24 °C and error estimation at different initial dye concentrations for 1HCl40 and raw algae (given in brackets).

<table>
<thead>
<tr>
<th>[MB]o (mg dm(^{-3}))</th>
<th>q(_e) calc. (mg g(^{-1}))</th>
<th>K(_1) (min(^{-1}))</th>
<th>R(^2)</th>
<th>( \chi^2 )</th>
<th>q(_e) (mg g(^{-1}))</th>
<th>K(_2) (g mg(^{-1}).min(^{-1}))</th>
<th>R(^2)</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.5</td>
<td>30.02</td>
<td>1.739</td>
<td>0.996</td>
<td>0.47</td>
<td>30.83</td>
<td>0.148</td>
<td>1</td>
<td>0.015</td>
</tr>
<tr>
<td>100</td>
<td>48.36</td>
<td>1.79</td>
<td>0.9977</td>
<td>0.77</td>
<td>49.1</td>
<td>0.149</td>
<td>1</td>
<td>0.06</td>
</tr>
<tr>
<td>150</td>
<td>72.73</td>
<td>2.185</td>
<td>0.996</td>
<td>2.1</td>
<td>73.73</td>
<td>0.1</td>
<td>0.999</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 5. The activation kinetic parameters for modified algae with 1M HCl (1HCl40) and raw algae (given in brackets).

<table>
<thead>
<tr>
<th>( E_a ) (kJ.mol(^{-1}))</th>
<th>( \Delta H^# ) (kJ.mol(^{-1}))</th>
<th>( \Delta S^# ) (kJ.mol(^{-1}).K(^{-1}))</th>
<th>( \Delta G^#_{298} ) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.8 (48.6)</td>
<td>41.9 (46.1)</td>
<td>-0.12 (-0.11)</td>
<td>77.7 (78.3)</td>
</tr>
</tbody>
</table>

The chemical modification by HCl did not affect strongly the activation thermodynamic parameters.
The activation thermodynamic parameters $E_a$, $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ were calculated. The equilibrium uptake is independent of isotherm adsorption temperature in the range studied ($25^\circ C – 35^\circ C$).

Acknowledgements
The authors wish to thank the “Ecole Doctorale de Sciences et Technologie” in Lebanese University for financial support.

REFERENCES


30. F. Luo, Y. Liu, Xiaomin Li, Z. Xuan, J. Ma, Biosorption of lead ion by chemically-modified biomass of marine brown algae Laminaria japonica, Chemosphere, 64, 2006, 1122-1127.


41. M. I. Temkin, Adsorption equilibrium and the kinetic of processes on non homogeneous surfaces and in the interaction between adsorbed molecules, Zh Fiz Chim., 15, 1941, 296- 332.

