



Research Journal of  
**Environmental  
Sciences**

ISSN 1819-3412



Academic  
Journals Inc.

[www.academicjournals.com](http://www.academicjournals.com)



## Research Article

# Protonated Biomass of the Brown Seaweed *Cystoseira tamariscifolia*: A Potential Biosorbent for Toxic Chromium Ions Removal

<sup>1</sup>Zahira Belattmania, <sup>1</sup>Samir El Atouani, <sup>1</sup>Soukaina Kaidi, <sup>2,3</sup>Fouad Bentiss, <sup>2</sup>Soufiane Tahiri, <sup>1</sup>Abdeltif Reani and <sup>1</sup>Brahim Sabour

<sup>1</sup>Phycology R.U-LB2VE, Department of Biology, Faculty of Sciences, Chouaïb Doukkali University, El Jadida, Morocco

<sup>2</sup>Department of Chemistry, Faculty of Sciences, Chouaïb Doukkali University, El Jadida, Morocco

<sup>3</sup>UMET-PSI, CNRS UMR 8207, National Graduate School of Engineering Chemistry of Lille, University of Lille1, Villeneuve d'Ascq Cedex, France

## Abstract

**Background and Objective:** Heavy metal pollution represents a serious problem with dramatic, ecological and human health consequences. This study aimed to investigate the hexavalent chromium (Cr(VI)) biosorption capacity of protonated biomass of the brown seaweed *Cystoseira tamariscifolia* (*C. tamariscifolia*). **Methodology:** *C. tamariscifolia* was harvested from the Atlantic coast of Morocco. The Cr(VI) removal from aqueous solutions by algal biomass were studied in a batch mode. Langmuir and Freundlich adsorption isotherms were applied to fit the experimental data. **Results:** Experimental results indicated that biosorption of Cr(VI) was highly pH dependent, favoring higher chromium removal at very low pH values. Equilibrium data were well fitted by Langmuir isotherm model with a maximum Cr(VI) uptake capacity ( $Q_{max}$ ) of 81.96 mg g<sup>-1</sup>. The kinetic models showed that biosorption process was perfectly described by a pseudo-second-order model. **Conclusion:** The protonated biomass of *C. tamariscifolia* seems to be a suitable low-cost biomaterial for removing hexavalent chromium from aqueous solutions.

**Key words:** Bioremediation, hexavalent chromium, protonated biomass, seaweed, *Cystoseira tamariscifolia*

**Citation:** Zahira Belattmania, Samir El Atouani, Soukaina Kaidi, Fouad Bentiss, Soufiane Tahiri, Abdeltif Reani and Brahim Sabour, 2018. Protonated biomass of the brown seaweed *Cystoseira tamariscifolia*: A potential biosorbent for toxic chromium ions removal. Res. J. Environ. Sci., 12: 106-113.

**Corresponding Author:** Brahim Sabour, Phycology R.U., Faculty of Sciences, Chouaïb Doukkali University, P.O. Box 20, 24000 El Jadida, Morocco  
Tel: +212523342325 Fax: +212523342187

**Copyright:** © 2018 Zahira Belattmania *et al.* This is an open access article distributed under the terms of the creative commons attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited.

**Competing Interest:** The authors have declared that no competing interest exists.

**Data Availability:** All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Contamination of aqueous environment by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain<sup>1</sup>. The effluents from metallurgical industries and mining sectors contain heavy metal ions, which are toxic to the living organisms<sup>2</sup>. Chromium is a highly toxic metal<sup>3</sup> and its presence in hexavalent form is one of the most important environmental problems due to the human health associated risk<sup>4</sup>. Most of effluent from electroplating, ferro-chromic and leather tanning industries contain higher Cr(VI) concentrations. Therefore, its removal from industrial effluents is necessary before their discharge into the recipient environment<sup>2</sup>. In general, toxic chromium ions are removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction and evaporation<sup>5</sup>. However, these methods have often some disadvantages such as secondary pollution, high chemical or energy requirements, high cost, leading a large number of scientists and environmentalists to develop more efficient removal processes for heavy metal remediation. Sorption is an emerging and innovative technology using different biomass to remove pollutants, especially heavy metals, from wastewater<sup>6,7</sup>. Among the biological materials, algae have been found to be potentially more suitable

sorbents because of their cheap availability both in fresh and marine waters, relatively high surface area and high binding affinity<sup>8</sup>. In this context, the present investigation aimed to evaluate the performance of protonated biomass of the brown seaweed *Cystoseira tamariscifolia* on toxic chromium ions removal and testing the effect of various parameters (pH, adsorbent dose, contact time and concentrations) on biosorption process.

## MATERIALS AND METHODS

**Sampling site and biosorbent preparation:** The brown seaweed *Cystoseira tamariscifolia* was collected at low tide in spring 2016 from the intertidal shoreline of El Jadida (33°14'41.8" N 8°32'27.8" W) on the Atlantic coast of Morocco (Fig. 1). To remove interfering ions and undesired materials (sand particles and debris), the algal biomass was washed with running tap water several times then by distilled water two time. The biomass was then sun dried for 3 days, thereafter, in an oven at 60°C for 24 h and subsequently referred as raw biomass. The protonated biomass was prepared as follow: 10 g of raw biomass was soaked into 1 L of 0.1 M HCl and stirred for 2 h at room temperature. The acidified biomass was then washed with distilled water and dried in an oven at 60°C for 24 h. Subsequently, it was ground to obtain a powder having an average particle diameter of about 500 µm.

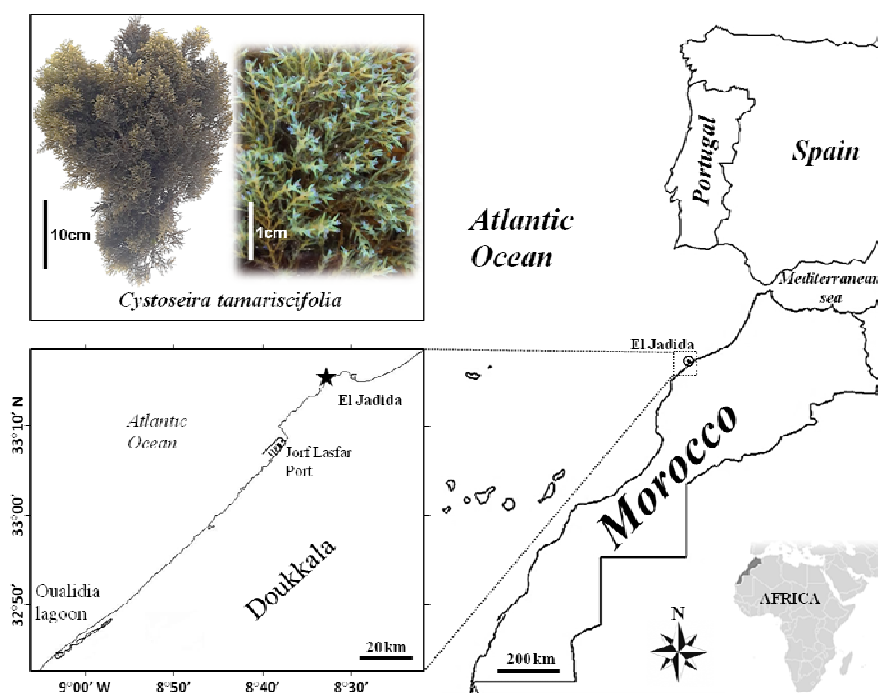


Fig. 1: Sampling site and illustrations of *Cystoseira tamariscifolia*

**FTIR characterization:** The identification of functional groups on the biosorbent surface was performed by Fourier transform infrared (FTIR) Spectroscopy using Thermo Scientific Nicolet iS50 Spectrometer over the wave number range 4000-600  $\text{cm}^{-1}$  in an attenuated total reflectance (ATR) mode. A total of 64 scans were averaged at 4  $\text{cm}^{-1}$  resolution and the IR spectra were then plotted and analysed.

**Preparation and analysis of chromium solution:** The chromium stock solution of desired concentration was prepared by solving calculated amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  in distilled water. The concentration of Cr(VI) ions in the solution was determined spectrophotometrically (UV-Visible Metashe 5200 HPC spectrophotometer) by developing a purple-violet color with 1,5-diphenylcarbazide in acidic solution as complexing agent. The absorbance of the purple-violet colored solution was read at 540 nm.

**Batch biosorption experiments:** The Cr(VI) biosorption by protonated biomass of *Cystoseira tamariscifolia* was performed in batch mode. For biosorption efficiency optimization, the experiments were conducted at pH values ranging from 2-9, different biosorbent dose (0.1-1.5 g/100 mL) and initial Cr(VI) concentrations from 10-500  $\text{mg L}^{-1}$ , in continuously stirred conical flasks containing 100 mL of chromium solution with contact time varying from 1-90 min. After equilibration time, samples were centrifuged at 4000 rpm for 20 min. The concentration of Cr(VI) ions in the supernatant solution was determined spectrophotometrically as previously described. The percentage removal and uptake capacity of Cr(VI) by the studied biomaterial were calculated using the equation:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

where,  $C_0$  and  $C_e$  were the initial and equilibrium concentrations of Cr(VI) ( $\text{mg L}^{-1}$ ).

**Statistical analysis:** All adsorption experiments were performed by triplicate. Microsoft Excel (Windows 10) was used to process experimental data and OMNIC 9.1 software for FTIR spectrum data.

## RESULTS AND DISCUSSION

**FTIR analysis:** The FTIR was used to analyze the functional groups in the protonated biomass of *Cystoseira tamariscifolia*. The obtained spectrum (Fig. 2) showed a broad band around 3300  $\text{cm}^{-1}$  corresponding to the stretching of hydroxyl (OH) and amine (NH) groups<sup>9</sup>. The peak observed at 2928  $\text{cm}^{-1}$  is indicative of the existence of  $\text{CH}_2$  asymmetric stretching vibration<sup>10</sup>. The peak around 1715  $\text{cm}^{-1}$  could be attributed to carboxylic acid ester (C=O) present in alginic acid<sup>11</sup>. The carboxyl ions were detected due to an asymmetrical stretching band<sup>12</sup> at 1622  $\text{cm}^{-1}$ . The band centered at 1515  $\text{cm}^{-1}$  could be assigned to the stretching of -NH groups. The band located around 1205  $\text{cm}^{-1}$  may be assigned to the presence of sulphate ester groups (S=O), mainly present in sulfonic acids of polysaccharides, such as fucoidan<sup>13</sup>. The strong band around 1025  $\text{cm}^{-1}$  was due to the C-O stretching of alcoholic groups<sup>12</sup>.

**Effect of solution pH:** The pH solution was regarded as the most important parameter controlling the practical use of

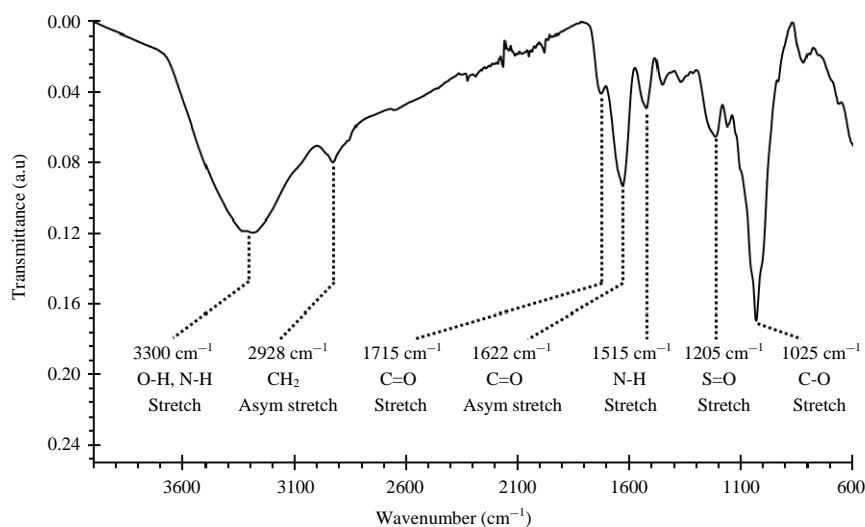


Fig. 2: Fourier transform infrared spectrum of *Cystoseira tamariscifolia* protonated biomass

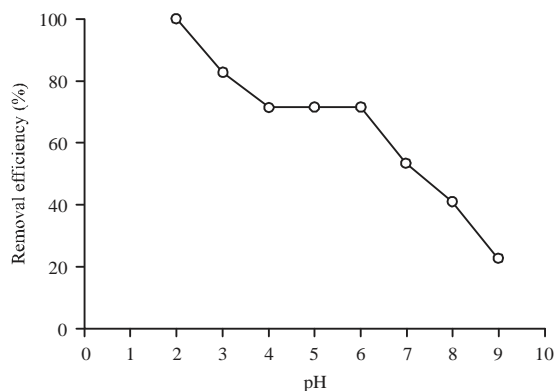


Fig. 3: Effect of pH on Cr(VI) removal by protonated biomass of *Cystoseira tamariscifolia*

nonliving biomass in the adsorption process<sup>2</sup>. The effect of pH on removal of hexavalent chromium by protonated biomass of *Cystoseira tamariscifolia* (Fig.3) showed that the maximum equilibrium uptake value was found at pH 2. Nonetheless, as the pH solution increases chromium removal efficiency decreases. Similar pattern was previously reported for the adsorption of chromium using raw algal biomasses<sup>2,14,15</sup>, residue recovered after biopolymer extraction<sup>16</sup> and chemically modified algal biomass<sup>9</sup>. At low pH values, the dominant species of hexavalent chromium ions in solution are  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Cr}_3\text{O}_{10}^{2-}$  and  $\text{Cr}_4\text{O}_{13}^{2-}$ . These chromate ion species could be adsorbed on the active sites of the protonated biomass, since the lower pH solution has a tendency to bind the protonated active sites of the biosorbent<sup>15,17</sup>. As the pH increased, the dominant species of hexavalent chromium ions in solution is  $\text{CrO}_4^{2-}$ . The decrease in adsorption of chromium ions with increase in the pH value may be due to the dual competition of both the anions  $\text{CrO}_4^{2-}$  and  $\text{OH}^-$  to be adsorbed on the surface of the adsorbent of which  $\text{OH}^-$  predominates<sup>18,19</sup>.

**Effect of sorbent dose:** The effect of adsorbent dose on the removal of Cr(VI) by the studied algal biomass (Fig. 4) demonstrated that the amount of adsorbent significantly influenced the level of metal ions adsorption which increased with increasing biomass dosage. The removal of chromium reaches its maximum (~100%) using biomass dose higher than 0.5 g/100 mL of hexavalent chromium solution at 50 mg L<sup>-1</sup>. This result may be due to the increase in the available binding sites in the biomass for the binding of heavy metal ions<sup>20</sup>.

**Effect of contact time:** The effect of contact time on chromium adsorption by treated seaweed *Cystoseira*

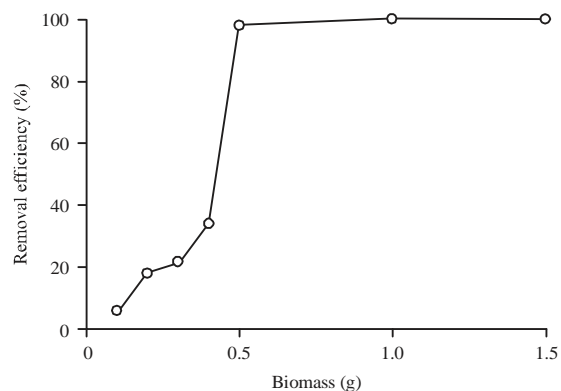


Fig. 4: Effect of biomass dosage on the Cr(VI) adsorption onto the protonated biomass of *Cystoseira tamariscifolia*

*tamariscifolia* was depicted in Fig. 5. As contact time increases, Cr(VI) uptake initially increases, then become almost stable, indicating attainment of equilibrium. Removal efficiency was fast during the first 10 min of contact time and thereafter, the sorption process reached equilibrium in about 30 min of contact time. The biosorption arisen in two steps, an initial rapid step which lasts for shorter time followed by the slower second part which continued until the equilibrium was reached. Further increase in contact time did not show any increase in chromium removal efficiency. Similar kinetic behavior has been achieved by Ullah *et al.*<sup>21</sup>. These changes in Cr(VI) uptake may be due to the fact that, initially, all adsorbent sites were unfilled and the solute concentration was high. After that, only a very low increase in the Cr(VI) uptake was observed because there were few surface active sites on the algal cell walls<sup>10</sup>.

**Biosorption kinetics:** Kinetics is one of the major parameters to evaluate biosorption dynamics and the kinetic constants can be used to optimize the residence time of a biosorption process<sup>22</sup>. To study the kinetics of Cr(VI) ions sorption onto *Cystoseira tamariscifolia* the pseudo-first order and pseudo-second order kinetics models were tested to fit the obtained experimental data.

The used linear form of the pseudo-first order kinetic equation was:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1 \times t}{2.303}$$

where,  $Q_e$  and  $Q_t$  are the biosorption capacity (mg g<sup>-1</sup>) at equilibrium and time  $t$ , respectively and  $K_1$  is the rate constant (L min<sup>-1</sup>) of pseudo first order kinetic model.

The pseudo-second order kinetics model equation can be written as:

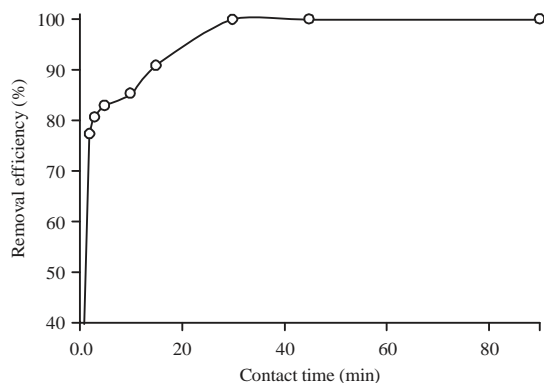


Fig. 5: Biosorption of Cr(VI) as a function of contact time

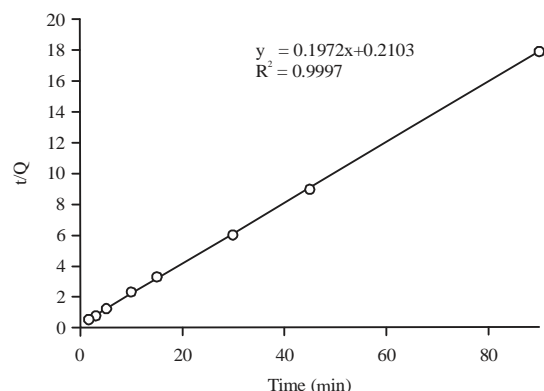


Fig. 7: Pseudo-second order kinetic model

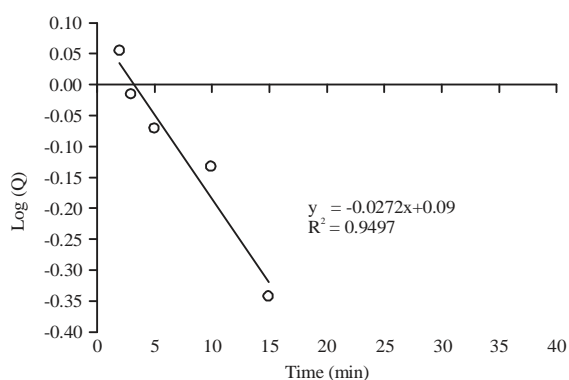


Fig. 6: Pseudo-first order kinetic model

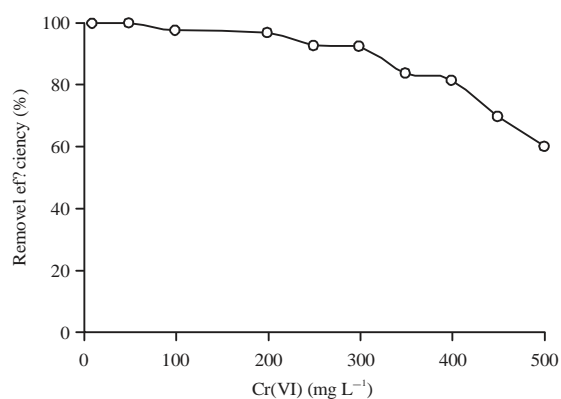


Fig. 8: Cr(VI) removal by *Cystoseira tamariscifolia* as a function of initial metal concentration

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2$$

Where:

t = The time (min)

$Q_t$  = The uptake capacity at a given time t ( $\text{mg g}^{-1}$ )

$Q_e$  = The equilibrium constant of sorbate ion on surface of the biosorbent ( $\text{mg g}^{-1}$ )

$K_2$  = The equilibrium rate constant of pseudo-second-order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ )

The results of the pseudo-first-order and pseudo-second order kinetic models were depicted in Fig. 6 and 7. The calculated values of respective parameters of first and second order kinetic models were summarized in Table 1. A comparison between pseudo-first-order and pseudo-second order kinetic models showed that the fit of the experimental data has led to correlation coefficients of 0.94 and 0.99 for pseudo-first and second order kinetic models, respectively. In the case of the first-order kinetics, the metal adsorbed amount at equilibrium determined experimentally (experimental  $Q_e$ ) clearly differed when compared to that deduced from the

model (calculated  $Q_e$ ). Definitely, it can be concluded that the pseudo-second order model provides the best fit for biosorption process which implies that the Cr(VI) removal involves various chemical interactions between functional groups and metal ions rather than their diffusion through boundary layers as dictated by pseudo-first order kinetic. This is in accordance with previous investigations on chromium removal by some biomaterials like the algal biomass of *Halopteris scoparia*<sup>23</sup> and the waste product of sugarcane bagasse<sup>21</sup>.

**Effect of metal concentration:** To study this parameter, the experiments were performed by varying initial chromium concentration from 10-500  $\text{mg L}^{-1}$  at an initial pH value of 2. The results (Fig. 8) showed that with an increase in Cr(VI) concentration, the removal efficiency decreases from 100% under both concentrations of 10 and 50  $\text{mg Cr(VI) L}^{-1}$  to 60.22% versus an extreme concentration of 500  $\text{mg Cr(VI) L}^{-1}$ . It is well known that initial concentration of metal ions greatly impacts the sorption capacity. They are adsorbed



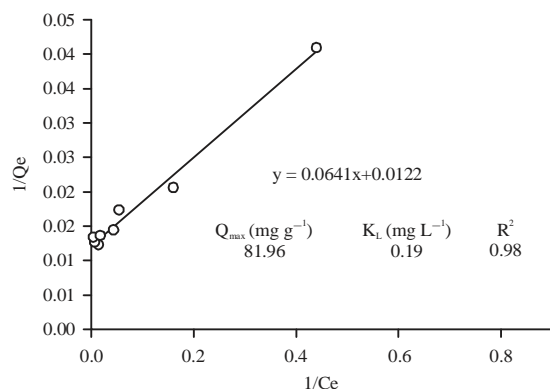


Fig. 9: Langmuir adsorption isotherm for Cr(VI) biosorption by *Cystoseira tamariscifolia*

Table 1: Kinetic parameters for Cr(VI) biosorption onto *Cystoseira tamariscifolia*

Parameters	Pseudo-first order	Pseudo-second order
K (g mg <sup>-1</sup> min <sup>-1</sup> )	-0.06	0.94
Q <sub>e</sub> experimental (mg g <sup>-1</sup> )	5.00	5.00
Q <sub>e</sub> calculated (mg g <sup>-1</sup> )	1.09	5.07
R <sup>2</sup>	0.94	0.99

on active sites while with more sorbate abundance all of them are inevitably filled and the sorbent increasingly saturated<sup>22</sup>.

**Modeling of adsorption isotherms:** Langmuir and Freundlich isotherm models were selected to fit the experimental data. The first one assumes a monolayer sorption of sorbate from the aqueous solution<sup>24</sup>. The Langmuir equation is given below:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_{max}} \times \frac{1}{C_e} + \frac{1}{Q_{max}}$$

Where:

- Q<sub>max</sub> (mg g<sup>-1</sup>) = Maximum biosorption capacity describing a complete monolayer adsorption
- Q<sub>e</sub> (mg g<sup>-1</sup>) = Amount adsorbed at equilibrium per specified amount of biosorbent
- C<sub>e</sub> = Equilibrium concentration of metal ion in solution
- K<sub>L</sub> = Adsorption equilibrium constant

The values of Q<sub>max</sub> and K<sub>L</sub> were respectively calculated from intercept and slope of linear plot of 1/Q<sub>e</sub> versus 1/C<sub>e</sub>.

The Freundlich equation was also employed to model equilibrium data of the biosorption process<sup>24,25</sup>. This model considers multi-layers adsorption on the sorbent surface. The linear form of Freundlich adsorption model is as follows:

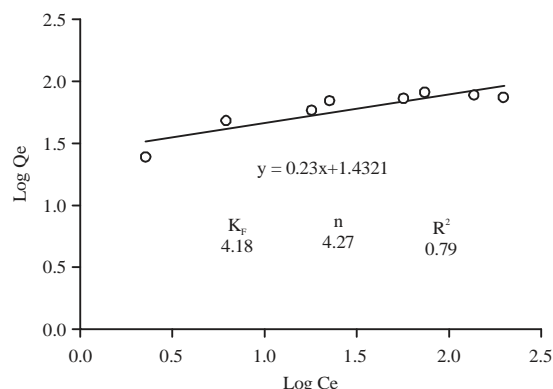


Fig. 10: Freundlich adsorption isotherm for Cr(VI) biosorption by *Cystoseira tamariscifolia*

Table 2: Maximum amount of Cr(VI) adsorbed at equilibrium/gram of *Cystoseira tamariscifolia* and other seaweeds

Seaweeds	Q <sub>max</sub> (mg g <sup>-1</sup> )	References
Raw <i>Oedogonium hatei</i>	31.0	Gupta and Rastogi <sup>1</sup>
Treated <i>Oedogonium hatei</i>	35.2	Gupta and Rastogi <sup>1</sup>
<i>Halimeda gracilis</i>	55.55	Jayakumar <i>et al.</i> <sup>26</sup>
<i>Gracilaria salicornia</i>	45.95	Khorramabadi and Soltani <sup>27</sup>
<i>Cystoseira indica</i>	20.9-27.9	Basha <i>et al.</i> <sup>10</sup>
<i>Sargassum</i> sp.	33.25	Khorramabadi and Soltani <sup>27</sup>
<i>Laminaria japonica</i>	59.35	Wang <i>et al.</i> <sup>28</sup>
<i>Sargassum muticum</i>	142.86	El Atouani <i>et al.</i> <sup>29</sup>
<i>Cystoseira tamariscifolia</i>	81.96	This study

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

Where:

- K<sub>F</sub> = Freundlich empirical constant relative to sorption capacity
- n = An empirical constant and rest of the terms have the usual significance

The values of K<sub>F</sub> and 1/n are obtained from the slop and intercept of the linear Freundlich plot of log Q<sub>e</sub> versus log C<sub>e</sub>.

Langmuir and Freundlich isotherms models were depicted in Fig. 9 and 10 as well as the regression correlation coefficient and the corresponding adsorption constants. It was observed that the correlation coefficient obtained by the use of Langmuir model was close to unity (R<sup>2</sup> = 0.98). In the case of Freundlich isotherm model, corresponding correlation coefficient (R<sup>2</sup> = 0.79) was low, which indicate that this model is not so adequately to describe the biosorption process of Cr(VI) onto *Cystoseira tamariscifolia* biomass. The Q<sub>max</sub> is an easily understandable value since it reflects the uptake potential of the sorption system and a useful parameter in scale-up considerations<sup>26</sup>. The calculated Q<sub>max</sub> (81.96 mg g<sup>-1</sup>)

suggests that the protonated biomass of *Cystoseira tamariscifolia* have an important absorption capacity when compared to other seaweeds (Table 2) such as the two green alga *Oedogonium hatei*<sup>1</sup> and *Halimeda gracilis*<sup>26</sup>, the red one *Gracilaria salicornia*<sup>10</sup> and the most brown seaweeds except the invasive *Sargassum muticum*<sup>29</sup> which exhibit a higher  $Q_{max}$  compared to the investigated algal biomaterial.

### CONCLUSION

In the present study, the removal of hexavalent chromium using protonated biomass of the brown alga *Cystoseira tamariscifolia*, harvested from the Moroccan Atlantic coast, was investigated. The FTIR spectroscopy of this biomaterial highlight the occurrence of some functional groups especially carboxyl, hydroxyl, amino and sulfonic groups which could contribute to Cr(VI) adsorption. Solution pH significantly influenced chromium biosorption and full removal obtained at more acidic pH values. The sorption process reaches the equilibrium at 30 min. The kinetic study shows that Cr(VI) biosorption can be described by pseudo-second-order model. The experimental results are well modeled according to the Langmuir adsorption isotherm. The maximum uptake capacity  $Q_{max}$  was also determined and is equal to  $81.96 \text{ mg g}^{-1}$ . These results gave evidence that biomass of *Cystoseira tamariscifolia* could be an appropriate low-cost material for removing hexavalent chromium from aqueous solutions.

### SIGNIFICANCE STATEMENT

This study discovers for the first time the remediation potential of *Cystoseira tamariscifolia* as a biological material for hexavalent chromium removal from aquatic solutions. The available biomasses of this fucoid along the Atlantic coast of Morocco, associated with its significant biosorption capacity, make this algal based sorbent a low-cost biomaterial for removing or reducing heavy metal pollution in aquatic environment. Future works must give emphasis on the strategies to be developed for a multiple biosorption-regeneration cycles to regenerate the biomass and eventually convert the recovered metal into usable form.

### ACKNOWLEDGMENTS

The authors are grateful to the anonymous reviewers for providing useful comments and suggestions that upgraded the manuscript. Zahira Belattmania acknowledges her

doctoral grant number 23691-09-14 awarded by the Ministry of Higher Education and Scientific Research of Morocco.

### REFERENCES

1. Gupta, V.K. and A. Rastogi, 2009. Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions. J. Hazard. Mater., 163: 396-402.
2. Baral, S.S., 2011. Seaweed as an Adsorbent to Treat Cr(VI)-Contaminated Wastewater. In: Handbook of Marine Macroalgae: Biotechnology and Applied Phycology, Se-Kwon, K. (Ed.), John Wiley and Sons, New York, pp: 461-477.
3. Netzahuatl-Munoz, A.R., M. del Carmen Cristiani-Urbina and E. Cristiani-Urbina, 2015. Chromium biosorption from Cr (VI) aqueous solutions by *Cupressus lusitanica* bark: Kinetics, equilibrium and thermodynamic studies. Plos One, Vol. 10. 10.1371/journal.pone.0137086.
4. Thatheyus, A.J. and D. Ramya, 2016. Biosorption of chromium using bacteria: An overview. Sci. Int., 4: 74-79.
5. Sen, M. and M.G. Dastidar, 2010. Chromium removal using various biosorbents. Iran. J. Environ. Health Sci. Eng., 7: 182-190.
6. Barros, A.J.M., S. Prasad, V.D. Leite and A.G. Souza, 2007. Biosorption of heavy metals in upflow sludge columns. Bioresour. Technol., 98: 1418-1425.
7. Mungasavalli, D.P., T. Viraraghavan and Y.C. Jin, 2007. Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*. Batch and column studies. Colloids Surf. A: Physicochem. Eng. Aspects, 301: 214-223.
8. Sari, A. and M. Tuzen, 2008. Biosorption of total chromium from aqueous solution by red algae (*Ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies. J. Hazard. Mater., 160: 349-355.
9. Yang, L. and J.P. Chen, 2008. Biosorption of hexavalent chromium onto raw and chemically modified *Sargassum* sp. Bioresour. Technol., 99: 297-307.
10. Basha, S., Z.V.P. Murthy and B. Jha, 2008. Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*. Chem. Eng. J., 137: 480-488.
11. El Atouani, S., F. Bentiss, A. Reani, R. Zrid and Z. Belattmania *et al.*, 2016. The invasive brown seaweed *Sargassum muticum* as new resource for alginate in Morocco: Spectroscopic and rheological characterization. Phycol. Res., 64: 185-193.
12. Bermudez, Y.G., I.L.R. Rico, E. Guibal, M.C. de Hoces and M.A. Martin-Lara, 2012. Biosorption of hexavalent chromium from aqueous solution by *Sargassum muticum* brown alga. Application of statistical design for process optimization. Chem. Eng. J., 183: 68-76.



13. Gomez-Ordóñez, E. and P. Ruperez, 2011. FTIR-ATR spectroscopy as a tool for polysaccharide identification in edible brown and red seaweeds. *Food Hydrocolloids*, 25: 1514-1520.
14. Murphy, V., H. Hughes and P. McLoughlin, 2008. Comparative study of chromium biosorption by red, green and brown seaweed biomass. *Chemosphere*, 70: 1128-1134.
15. Belattmania, Z., S. Tahiri, R. Zrid, A. Reani and S. Elatouani *et al.*, 2015. Bioremoval of hexavalent chromium from aqueous solutions by the brown seaweed *Dictyopteris polypodioides*. *Res. J. Environ. Toxicol.*, 9: 218-230.
16. Belattmania, Z., S. Tahiri, F. Bentiss, A. Sahibed-Dine and C. Jama *et al.*, 2017. The residue of alginate extraction from *Sargassum muticum* (brown seaweed) as a low-cost adsorbent for hexavalent chromium removal from aqueous solutions. *Desalin. Water Treat.*, 75: 107-114.
17. Aksu, Z., U. Acikel, E. Kabasakal and S. Tezer, 2002. Equilibrium modelling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge. *Water Res.*, 36: 3063-3073.
18. Donmez, G. and Z. Aksu, 2002. Removal of chromium(VI) from saline wastewaters by *Dunaliella* species. *Process Biochem.*, 38: 751-762.
19. Gupta, S. and B.V. Babu, 2009. Removal of toxic metal Cr (VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies. *Chem. Eng. J.*, 150: 352-365.
20. Oboh, I., E. Aluyor and T. Audu, 2009. Biosorption of heavy metal ions from aqueous solutions using a biomaterial. *Leonardo J. Sci.*, 14: 58-65.
21. Ullah, I., R. Nadeem, M. Iqbal and Q. Manzoor, 2013. Biosorption of chromium onto native and immobilized sugarcane bagasse waste biomass. *Ecol. Eng.*, 60: 99-107.
22. Babu, D.J., B. Sumalatha, T.C. Venkateswarulu, K.M. Das and V.P. Kodali, 2014. Kinetic, equilibrium and thermodynamic studies of biosorption of chromium (VI) from aqueous solutions using *Azolla filiculoides*. *J. Pure Applied Microbiol.*, 8: 3107-3116.
23. Belattmania, Z., R. Zrid, A. Reani, S. Tahiri and A. Eddaoui *et al.*, 2015. Phycoremediation of hexavalent chromium in simulated wastewater by *Halopteris scoparia* (Linnaeus) Sauvageau (Ochrophyta, Phaeophyceae). *J. Mater. Environ. Sci.*, 6: 2229-2238.
24. Lawal, O.S., A.R. Sanni, I.A. Ajayi and O.O. Rabi, 2010. Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*. *J. Hazard. Mater.*, 177: 829-835.
25. Freundlich, H., 1907. Ueber die Adsorption in Loesungen. *Z. Phys. Chem.*, 57: 385-470.
26. Jayakumar, R., M. Rajasimman and C. Karthikeyan, 2014. Sorption of hexavalent chromium from aqueous solution using marine green algae *Halimeda gracilis*: Optimization, equilibrium, kinetic, thermodynamic and desorption studies. *J. Environ. Chem. Eng.*, 2: 1261-1274.
27. Khorramabadi, G.S. and R.D.C. Soltani, 2008. Evaluation of the marine algae *Gracilaria salicornia* and *Sargassum* sp. for the biosorption of Cr (VI) from aqueous solutions. *J. Applied Sci.*, 8: 2163-2167.
28. Wang, X.S., Z.Z. Li and C. Sun, 2008. Removal of Cr(VI) from aqueous solutions by low-cost biosorbents: Marine macroalgae and agricultural by-products. *J. Hazard. Mater.*, 153: 1176-1184.
29. El Atouani, S., S. Tahiri, A. Reani, F. Bentiss and M. El Krati *et al.*, 2016. Hexavalent chromium uptake from aqueous solutions using raw biomass of the invasive brown seaweed *Sargassum muticum* from the Moroccan shorelines: Kinetics and isotherms. *Eur. Scient. J.*, 12: 243-262.