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Fucus vesicuolsus SURFACE MODIFICATION FOR ENHACED BIOSORPTION OF METHYLENE BLUE: EQUILIBRIUM STUDIES

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ABSTRACT – Dyes and pigments are widely used in the textile, food, paper and cosmetics industries, and for this reason a huge amount of effluent is generated in these segments. Without proper treatment, the discharge of these effluents is associated with several environmental problems and has been a major concern over the years. Thus, this study evaluated a type of brown macroalgae (*Fucus vesiculosus*) and its modification with sodium hydroxide for methylene blue biosorption. The biosorbent characterization revealed as major components carbon and oxygen, lipids and proteins were also observed. For both biosorbent (unmodified and modified) the Langmuir model presented the best fit for the experimental data, revealing a maximum adsorption capacity of 698.47 $mg \cdot g^{-1}$ and 818.16 $mg \cdot g^{-1}$ for unmodified and modified biosorbent.

1. INTRODUCTION

Increasing pollution is one of the major problems that our ecosystem is facing both at the aquatic and the terrestrial level. Some of the sources of polluting agents include chemical byproducts, herbicides, pesticides, pharmaceuticals, cosmeceuticals, leather, textiles, the plastic industry, pigments, electroplating, storage batteries, mining, smelting, metallurgical processes, nanoparticles, etc. (Cazón and Donati, 2018). In recent years, sorption technology has received attention for dye remediation owing to its simple operational condition that promotes cost-effectiveness, eco-friendliness and eco-safety (Lee *et al.*, 2017). The development of green and low-cost adsorbent has increased interest among researchers since the application of commercial adsorbent such as activated carbon has several limitations, namely due to their high production cost and poor regeneration ability (Oguntimein, 2015). Another material class that has shown promise in these compounds' remediation are the algae. Whether macro or microalgae, algae have several advantages over conventional treatment forms used for dye remediation. In addition to their high removal capacity, algae are easily obtained, and their cultivation takes place both in fresh and salt water under different climatic conditions (Lebron *et al.*, 2018).

Thus, this study aimed to evaluate the methylene blue biosorption isotherms for a specie of brown macro algae (*Fucus vesiculosus*) and the activation process with sodium hydroxide (NaOH) influence over its biosorption capacity.

2. MATERIALS AND METHODS

The biosorption experiments were performed in duplicate, using modified and unmodified *F. vesiculosus* dried biomass. The biosorbent samples were stored in the absence of light and humidity prior to their use. All reagents used were analytical grade and the solutions prepared in ultrapure water (ThermoScientific Smart2Pure 3 UV).

2.1 *Fucus vesiculosus* activation and characterization

Part of the algae sample was chemically modified in 50 mL solution at a 1:2 mass ratio of biomass to sodium hydroxide (NaOH). The system was kept in a shaker (Marconi MA420) under constant agitation (250 rpm) and temperature (28 ºC) for 24h. After that, the sample was filtered and washed with distilled water until a neutral pH. The remaining water was removed in a drying oven at 105 ºC for 2 h, followed by a grinding step in a Wiley mill (Tecnal, TE-680) until it reached a particle size smaller than 250 µm.

The modified and unmodified algae samples were analyzed for their morphology and composition by scanning electron microscopy (SEM) coupled to X-ray dispersive energy (EDS) (JEOL JSM IT300) and ATR-FTIR (Shimadzu IRAffinity-1).

2.2. Biosorption experiments

The experiments were conducted in media containing 2 $g \cdot L^{-1}$ of biosorbent and varied concentration of methylene blue (100 - 2000 $mg \cdot L^{-1}$). The system was kept under constant agitation (250 rpm) and temperature (28 ºC) for 4 h, enough time to ensure the equilibrium. Then, aliquots were collected and filtered using a 0.45 µm PVDF syringe filter (CHROMAFIL® Xtra) to determine the equilibrium concentration with the aid of a molecular absorption spectrophotometer (Shimadzu UV 3600) and an external calibration curve (R^2 = 0.99). The algae sample biosorption capacity q_e ($mg \cdot g^{-1}$) was determined by Equation 1, where C_0 ($mg \cdot L^{-1}$) and C_e ($mg \cdot L^{-1}$) corresponds to the initial and equilibrium concentration, respectively, v (L) to the medium volume and m (g) to the biosorbent mass.

$$q_e = v(C_0 - C_e)/m \quad (1)$$

The equilibrium was evaluated by four different models proposed by Langmuir, Freundlich, Dubinin-Radushkevich and Temkin, presented in Equations 2 – 5 in their non-linear form, respectively. They were chosen based on their ability to describe the process and enabling a better comprehension in terms of biosorption capacity, single or multiple layers formation of adsorbate over the biosorbent surface, binding energy involved, among others. The estimations were made using OriginLab®, minimizing the chi-square function using the Levenberg–Marquardt (L-M) algorithm.

$$q_e = q_m k_L C_e/(1 + k_L C_e) \quad (2)$$

$$q_e = k_F C_e^{1/n} \quad (3)$$

$$q_e = q_s exp\{-K_{DR}[RTln(1 + 1/C_e)]^2\} \quad (4)$$

$$q_e = (RT/b)\ln(A_T C_e) \quad (5)$$

Where q_m (mg·g^{-1}) is the Langmuir maximum biosorption capacity, k_L (L·mg^{-1}) is the Langmuir equilibrium constant, k_F (mg$^{1-1/n}$·L$^{1/n}$·g^{-1}) and n are constants related to Freundlich model, q_s (mg·g^{-1}) is the theoretical saturation capacity obtained by Dubinin-Radushkevich model, K_{DR} (mol^2·J^{-2}) is the Dubinin-Radushkevich isotherm constant, R (8.314 J·mol^{-1}·K^{-1}) is the ideal gas constant, T (K) is the absolute temperature, b (J·mol^{-1}) is Temkin's isotherm constant related to the adsorption heat, and A_T (L·g^{-1}) is the Temkin isotherm equilibrium biding constant. The reliability of the model fitted was evaluated by the correlation coefficient (R^2) (Equation 6) and the average relative error (ARE) function (Equation 7).

$$R^2 = \sum\left(q_{exp} - \overline{q_{exp}}\right)^2 - \sum\left(q_{exp} - q_{cal}\right)^2 / \sum\left(q_{exp} - \overline{q_{exp}}\right)^2 \quad (6)$$

$$ARE\ (\%) = (100/N)\sum\left|\left(q_{exp} - q_{cal}\right)/q_{exp}\right| \quad (7)$$

In which q_{exp} (mg·g^{-1}) corresponds to the experimental biosorption capacity, $\overline{q_{exp}}$ (mg·g^{-1}) is the experimental data mean, q_{cal} (mg·g^{-1}) to the values predicted by the models, and N to the sample size.

3. RESULTS AND DISCUSSION

3.1 Fucus vesiculosus activation and characterization

Surface modification due to the activation process was confirmed by the shift in the ATR-FTIR absorption bands (Figure 1). Among the bands observed are those between 1800 and 900 cm^{-1}, corresponding to lipids, proteins, and carbohydrates (Mecozzi *et al.*, 2008). The images obtained by scanning electron microscopy revealed a biosorbent with a non-homogeneous and irregular surface, which favors the biosorption process due to the greater surface area availability (Figure 2 a,b). Carbon and oxygen are the majors compound found in the biosorbents samples (Figure 2 c,d), derived from the biomolecules mentioned above.

Figure 1 –ATR-FTIR before and after the pretreatment process.

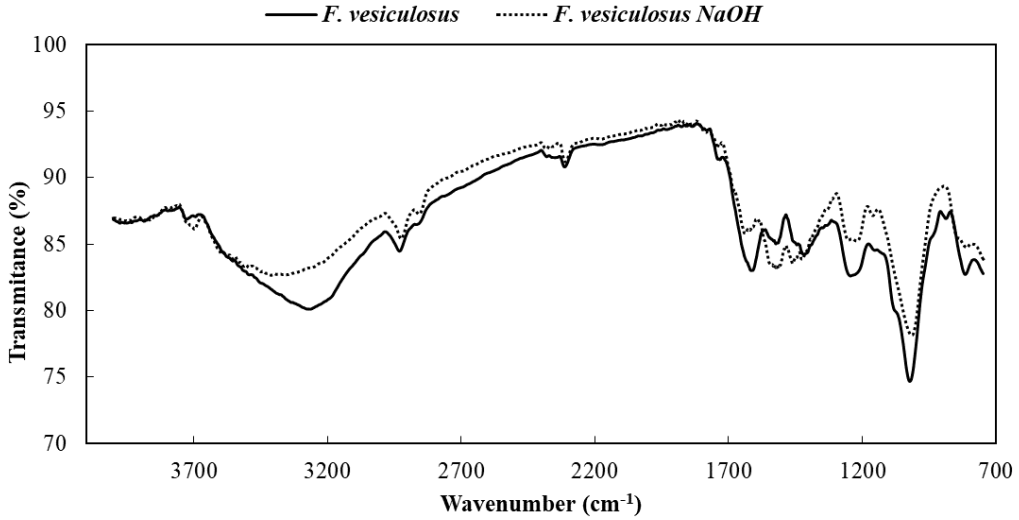
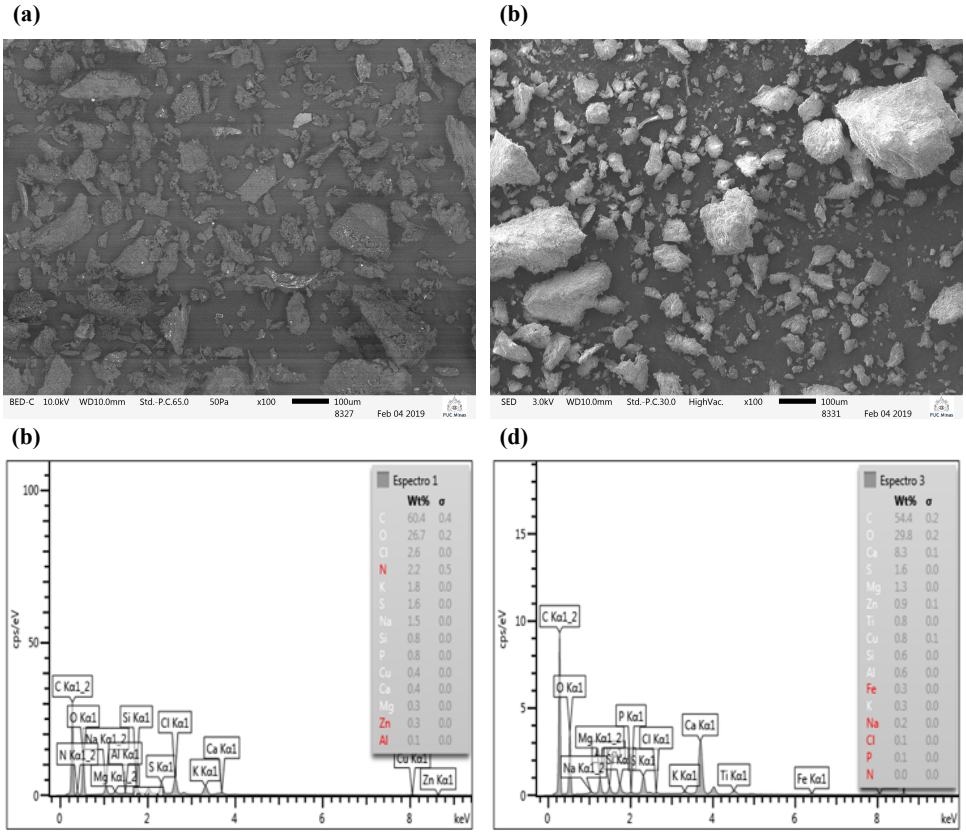


Figure 2 – Scanning electron microscope images at magnification 100x for the (a) unmodified and (b) modified algae samples, and X-Ray dispersive energy for elemental composition for the (c) unmodified and (d) modified samples.



3.2 Fucus vesiculosus equilibrium studies

The results concerning the equilibrium parameters obtained for the different models are presented in Figure 3 and Table 1. Among those, Langmuir presented the highest R^2 and lower *ARE* (%), demonstrating the best fit for both algae sample. For the unmodified, the maximum biosorption capacity was 698.47 mg·g^{-1}, while for modified algae sample the biosorption capacity increased by 17.13 % (818.16 mg·g^{-1}). In both cases the process was classified as favorable since the separation coefficient (R_L) was between 0 – 1 (Lebron *et al.*, 2018). Likewise, Freundlich constant n was contained within the range of 1 - 10, reassuring the results obtained. Therefore, small quantities of *F. vesiculosus* can adsorb significant methylene blue amounts. In spite of the fact that Langmuir model was chosen for the process description, Temkin isotherm satisfactorily adjusted to the experimental data, which allows a better comprehension of the process. The constant b obtained in both algae samples could be considered low, characterizing a process governed by physical interactions. This confers an advantage to the process considering that the biosorbent regeneration would be easier, therefore allowing its reusability in subsequent treatment processes. Furthermore, the Dubinin-

Radushkevich isotherm allows the understanding of the nature involved in the biosorption process as it is commonly used to differentiate a physical from a chemical biosorption process by the "*E*" values obtained (Do Nascimento *et al.*, 2014). For values of "*E*" smaller than 8 kJ mol^{-1} there is a predominance of physical interaction, while values between 8 and 16 kJ mol^{-1} suggest chemical interaction (Mitrogiannis *et al.*, 2015). In this study, the calculated "*E*" indicated a predominance of physical interactions for unmodified *F. vesiculosus* and a predominance of chemical interaction in the modified *F. vesiculosus.*

Figure 3 – Equilibrium isotherms for methylene blue biosorption onto modified and unmodified *Fucus vesiculosus.*

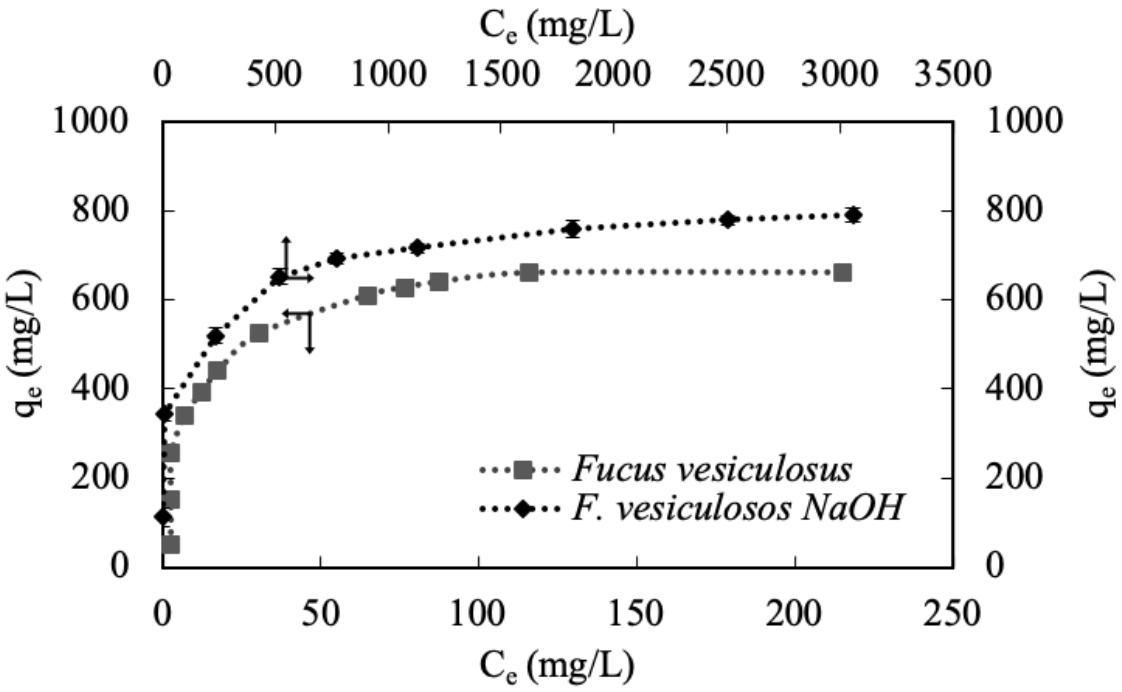


Table 1 – Equilibrium parameters regarding the methylene blue biosorption. [a] Expressed in ($mg^{1-1/n} \cdot L^{1/n} \cdot g^{-1}$)

Langmuir	**Unmodified**	**Modified**	**Dubinin-Radushkevich**	**Unmodified**	**Modified**
q_m ($mg \cdot g^{-1}$)	698.47 ± 14.25	818.16 ± 5.14	K_{DR} ($mol^2 \cdot J^{-2}$)	603.63 ± 28.43	363.22 ± 0.65
k_L ($L \cdot mg^{-1}$)	0.11 ± 0.01	0.0073 ± 0.0003	q_s ($mg \cdot g^{-1}$)	7.28 ± 1.99	752.94 ± 15.40
$R_{L,min-max}$	0.071 - 0.773	0.03 - 0.11	E ($kJ \cdot mol^{-1}$)	0.26	11.71
R^2	0.996	0.995	R^2	0.770	0.889
ARE (%)	1.317	0.761	*ARE* (%)	10.942	4.509
Freundlich			**Temkin**		
n	4.28 ± 11.76	7.01 ± 0.93	A_T ($L \cdot g^{-1}$)	0.02 ± 0.56	1.03 ± 0.73
k_F [a]	225.30 ± 0.23	258.06 ± 34.87	b ($g \cdot J \cdot mg^{-1} \cdot mol^{-1}$)	2.38 ± 0.29	24.96 ± 2.51
R^2	0.985	0.927	R^2	0.980	0.952
ARE (%)	2.311	3.699	*ARE* (%)	2.959	2.991

4. CONCLUSIONS

Considering the impacts caused by the presence of dyes in the environment, the methylene blue biosorption from aqueous solution by the brown algae *Fucus vesiculosus* was investigated. The biosorbent presented a non-homogeneous surface, composed mainly of carbon and oxygen. The equilibrium was best described Langmuir's model, suggesting a monolayer formation over the biosorbent surface. An increase in binding energy can be observed for the modified *F. vesiculosus* from the parameter "*b*" and "*E*" from the Temkin and Dubinin–Radushkevich isotherm models, respectively. Indicating a predominance of physical interactions for unmodified *F. vesiculosus* and a predominance of chemical interaction in the modified *F. vesiculosus*. Lastly, after the activation process with NaOH, the biosorbent presented a 17.13 % increase in its maximum adsorption capacity, demonstrating the pretreatment efficiency on the biosorbent uptake capacity.

5. REFERENCES

CAZÓN, Josefina Plaza; DONATI, Edgardo. Biosorption of Dyes by Brown Algae. Strategies for Bioremediation of Organic and Inorganic Pollutants, *Boca Raton: CRC Press*. p. 1884, 2018.

DO NASCIMENTO, Ronaldo Ferreira *et al.* Adsorção: aspectos teóricos e aplicações ambientais. Biblioteca de Ciências e Tecnologia, 2014.

LEBRON, Y. A. R. *et al.* Remediation of methylene blue from aqueous solution by Chlorella pyrenoidosa and Spirulina maxima biosorption: Equilibrium, kinetics, thermodynamics and optimization studies. *Journal of Environmental Chemical Engineering*, v. 6, p. 6680-6690, 2018.

LEE, Wei-Kang *et al.* Biosynthesis of agar in red seaweeds: A review. *Carbohydrate polymers*, v. 164, p. 23-30, 2017.

MECOZZI, M. *et al.* Characterization of a bioassay using the marine alga Dunaliella tertiolecta associated with spectroscopic (visible ad infrared) detection. *International Journal of Environmental Pollution*, v. 32, n. 1, p.104-120, 2008.

MITROGIANNIS, Dimitris et al. Biosorption of methylene blue onto *Arthrospira platensis* biomass: kinetic, equilibrium and thermodynamic studies. *Journal of Environmental Chemical Engineering*, v. 3, n. 2, p. 670-680, 2015.

OGUNTIMEIN, Gbekeloluwa B. Biosorption of dye from textile wastewater effluent onto alkali treated dried sunflower seed hull and design of a batch adsorber. *Journal of Environmental Chemical Engineering*, v. 3, n. 4, p. 2647-2661, 2015.