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Potential of brown algae biomass as new biosorbent of Iron: Kinetic, equilibrium and thermodynamic study

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Abstract

The brown alga *Sargassum Vulgare* was used as biosorbent for Fe^{3+} ions removal in aqueous solution. The biosorption studies of the algae biomass were executed in batch system. The biosorbent was characterized using FTIR, SEM, BET and elemental analysis. Several parameters were inspected in order to find the optimum biosorption conditions of Fe^{3+} removal as a function of pH, contact time, biomass dosage and initial metal concentration. Langmuir and Freundlich isotherms were found applicable in terms of relatively high regression values. The maximum adsorption capacity of the biosorbent obtained from the Langmuir adsorption isotherm was found about 19.86 mg/g, at 120 min contact time, pH=2, 5 g/L algae dosage, and 298K temperature.The thermodynamic parameters of the process (ΔG, ΔH and ΔS) were estimated from tests carried out at different temperatures (298, 308 and 318 K). The Kinetics of sorption followed the first order model. The Gibbs free energy and the enthalpy were negative ($-5.69<\Delta G<-3.16$kJ/mol; $\Delta H = -23.24$kJ/mol) indicate that the biosorption was a spontaneous and exothermic process. FT IR results of algal biomass indicate that biomass has different functional groups able to react with metal ion in aqueous solution. The Biosorbent could be regenerated three times using 0.001M EDTA solution, with 94% recovery.

1. Introduction

The increasing of wastewater pollution is caused by the intense industrial activities which generate large quantities of aqueous effluents containing several toxic products, such as heavy metals, dyes, pesticides, phenols, organic pollutants[1]. The presence of heavy metals such as cadmium, chromium, lead, zinc, and iron with a high or low concentration has been recognized as harmful to natural ecosystem and human life. Heavy metals are considered causing toxic effects, cancer and diseases because, they are not degradable [2,3]Among different metals , the presence of iron in water with high concentration can affect water quality, chemistry, cause damage to the human body, affect the root system and growth of various wetland and river ecosystem species depending upon their tolerance mechanism [4]. Various techniques have been used for the removal of wastewater pollution, such as coagulation, advanced oxidation, membrane separation [5]and electrodialytic[6]. However, the biosorption is the most effective process, due of their high effectiveness, low cost, simplicity and capacity to regenerate the biosorbent [7–10].

Many studies reveal that the marine algae, are one of the most important biosorbent, with a high recovery for various metals, which results from the presence of different functional groups in their cell wall, such as hydroxyl, carboxyl, amino and phosphate that have an important role in the removal of toxic pollutants from different industrials effluents [11–14]. Among three types of marine algae (red, green, brown), brown algae has been found to be very effective biosorbent in removing heavy metals [15–17] because of their high ability resulting from the composition of cell wall which includes alginate, chitin, lipids, polysaccharides and proteins [3,18]

Our region is located in the north of Morocco, the physicochemical characterization and statistical analysis of total metal concentration of greases and wastewater samples from two wastewater treatment plants in

Tangier and Tetouan, indicate that the several industries reject a large amount of wastewater, containing different metals such as chrome, copper and iron with higher concentration [19]. Furthermore, the competition with metals in solution is one of the most problems for industrial wastewater treatment. The cost is characterized by the abundance of the brown macroalgae, which considerate as low cost and effective biosorbent of wastewater treatments. The aim of the present study was to investigate the potential of brown algae *Sargassum Vulgare* on the biosorption of Fe^{3+} before starting the treatment in competition with other metals. The experiments were done in a batch system. The Different effects influencing the Iron removal were studied essentially, the effect of pH, initial metal concentration, kinetics, equilibrium sorption, thermodynamic and desorption.

In addition, various models parameters have been utilized for describing the biosorption process. To the best of our knowledge, *Sargassum Vulgare* biomass was used here for the first time for Fe^{3+} removal and it was observed that the proposed biomass is effective in terms of its performance.

2. Materials and methods

2.1. Biomass Preparation

The macroalgae biomass *Sargassum Vulgare* was used in this study as biosorbent of Fe^{3+}. The brown algae were collected in the cost of Tetouan (NW Morocco). The collected sample was washed several times with tap and deionized water to remove impurities, and then was sun dried for 48h and in oven at 60°C for 24h. The biomass was crushed and sieved to particle size 0.5 mm, then stored in polyethylene bottles until their use.

2.2. Characterization of algae biomass

Scanning Electron Microscopy (SEM) characterized the surface morphology of dried algae biomass. A Fourier Transform Infrared (Bruker Vertex 70 FT-IR spectrophotometer) was used to determine the main functional groups present on the surface biomass. The surface area of the biosorbent was measured by Brunauer–Emmett–Teller (BET) method (Micromeritics ASAP 2020) using nitrogen as the adsorbate. The elemental analysis (C, H, N, S, and O) of the algae biomass was performed using Perkin Elmer CHNSO 2400 apparatus. The concentrations of metal ions were measured by using Varian SpectrAA 110 Atomic Absorption Spectrometer Atomic (AAS).

2.3. Biosorption experiments

A stock solution of Fe^{3+} was prepared at the concentration of 1 g/L using $Fe\ NH_4\ (SO_4)_3\ 12H_2O$ in deionized water. The pH was controlled to target value using 0.1M solutions of H_2SO_4. The batch experiments of Fe^{3+} biosorption on *Sargassum* biomass were carried out in glass bottle by mixing an amount of algae biomass with 100 ml of a fixed iron concentration. The suspension was maintained under a stirring at 100 rpm and 298 K for 180 min. Fe^{3+} solution was adjusted to different pH values (1.5, 2.0, 2.5, and 3.0). The effect of the initial metal concentration was investigated by adding a constant amount of biomass (5 g/L) to a series of glass bottles containing iron solution (25, 50, 75 and 100 mg/L), the solutions were shaked for 180 min at 298 K until is equilibrium. Samples were analyzed every 5 and 10 min during the first hour, and every 30 min during the remaining 2h. The influence of biomass dosage ranging from 1 to 10 g/L was also studied by keeping others parameters constant. For the kinetics of sorption, the same amount of biosorbent (5 g/L) was mixed with 100 mL of iron metal solution (50 mg/L) at 298 K for predetermined intervals of time. Equilibrium experiments were performed with 25 mL of various iron initial concentrations ranging from 3 to 100 mg/L that were mixed with 5 g /L biomass dosage at 298 K temperature. The solutions were shaked for 120 min. In order to determine the various thermodynamic parameters, 298, 308 and 318 K temperatures were used to conduct biosorption experiments. The biosorption capacity was calculated through the following equation[20]

$$q = \frac{C_i - C_f}{M} \times V$$

Where q is the amount of metal adsorbed per gram of the adsorbent (mg /g). C_i and C_f are the initial and final concentrations (mg/L) of the metal ions. V is the volume of the aqueous solution (L) and M is the amount of the biosorbent (g). Each experiment was repeated 2 times and the given results are the average values. The iron removal was calculated from the following equation:

$$\%\,Removal = \frac{C_i - C_f}{C_i} \times 100$$

2.4. Isotherm models

Biosorption process is a mass transfer operation that can be described mathematically by an equilibrium process and a rate process. Sorption isotherm represents the distribution of the solute at equilibrium between the solid phase (sorbent) and the aqueous phase (solution). In this study two isotherms Langmuir and Freundlich models were investigated to analyze the equilibrium data. The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneous biosorption energy. The mathematics of this model was expressed as the following equation:

$$q_e = \frac{(q_m k_L C_e)}{1 + (k_L C_e)}$$

q_e is the metal uptake capacity (mg/g) and C_e is the equilibrium concentration of metal ions in the solution (mg/L), q_m is the biosorption capacity when the surface is completely covered with metal ions (maximum biosorption capacity), and k_L (L/mg) is a constant that represents the affinity between the biosorbent and the metal ion.

The heterogeneity of the surface and multilayer biosorption to the binding sites located on the surface of the biosorbent are considered in the Freundlich isotherm which is an empirical expression and expressed as:

$$q_e = k_f C_e^{1/n}$$

Where k_f and *n* are the Freundlich characteristic constants of the system K_f (L/g) and *n* are the indicator of the biosorption capacity and biosorption intensity, respectively.

2.5. Kinetic modeling

In order to investigate the mechanism of heavy metals biosorption onto *Sargassum* biomass, the pseudo-first order and pseudo-second model were used to fit the kinetic experimental data. According to the following equations, the pseudo-first order model describes the rate of biosorption to be proportional to the number of sites unoccupied by the solutes [21]:

$$q_t = q\,(1 - exp^{-k_1 t})$$

Where q_t and q are the metal ion concentrations (mg/g) at time (t) and at the equilibrium, respectively, and k_1 is the first order rate constant (min^{-1}).

The pseudo-second order kinetic model was represented as the following equation [22]:

$$q_t = \frac{q^2 \mathrm{K}_2 \mathrm{t}}{1 + q\,K_2\,t}$$

Where k_2 is the pseudo second-order rate constant (g/mg/min). The experimental data was fitted by MATLAB software. In addition to the correlation coefficient (R^2), the residual root mean square error (RMSE) value was also evaluated for better fit of model:

$$RMSE = \sqrt{\frac{1}{N-p} \sum_{i=1}^{m} (q_{-} q_m)^2}$$

q is the observation from batch experiment, q_m is the measured value from the isotherm for corresponding q_e, N is the number of observation in the experimental design, and p is the number of parameters to be determined. Smaller value of RMSE and high value of correlation coefficient indicate a better fit of model [23].

2.6. Biosorption thermodynamics

The thermodynamics of the biosorption of Fe^{3+} onto dried *Sargassum vulgare* was evaluated at different temperatures (298, 308 and 318 K) under constant conditions, specifically 5g/L biomass, 50 mg/L initial metal concentration, pH= 2 and stirring speed at 100 rpm. The main thermodynamic parameters including changes in the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were used to assess the spontaneity and endo-or exothermic nature of the biosorption process as the following equations [24].

$$\Delta G = -RTlnk_D$$
$$\Delta G = \Delta H - T\Delta S$$

Where K_D (q_e/C_e) is the distribution coefficient.

2.7. Desorption study

In order to determine the reusability of algae biomass, three consecutive adsorption-desorption cycles were performed. Desorption of Fe^{3+} ions was performed by 0.1M HCl, 0.1M HNO_3, and 0.001 M EDTA solutions. The biomass loaded with Fe^{3+} ions was placed in the desorption medium and stirred at 100 rpm for 120 min at 298K. The final metal concentration in the aqueous phase was determined by AAS. After each cycle of adsorption–desorption, biomass was washed with distilled water and reconditioned for the succeeding cycle. The desorption ratio was calculated from the amount of metal ions adsorbed and the final Fe^{3+} ion concentration in the adsorption medium. Desorption ratio was calculated from the following equation:

$$\text{Desorption} = \frac{Amount\ of\ metal\ ions\ desorbed}{Amount\ of\ metal\ ions\ adsorbed} \times 100$$

3. Results and discussion

3.1. Characterization of Sargassum Vulgare

The surface area of the algae biomass *Sargassum Vulgare* was observed to be 0.126 m^2/g by BET method. The biosorbent was also subjected to elemental analysis and the results are summarized in Table 1.

Table 1: Physicochemical properties

Parameters	Value
Carbon, % (w/w)	33.347
Oxygen, % (w/w)	48.86
Hydrogen, % (w/w)	4.963
Nitrogen, % (w/w)	0.498
Sulphur, % (w/w)	0.078
S_{BET} (m^2/g)	0.1265

The FTIR technique was used to identify the functional groups presence before and after Fe^{3+} ions biosorption, and the results are shown in Fig.1.

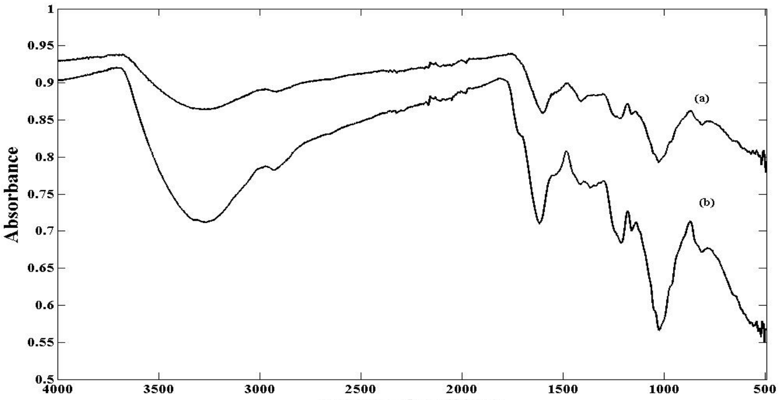

Figure 1: FT-IR spectra of Sargassum Vulgare before (a) and after (b) metal loading

The observed stretching in algae FTIR spectra are given in Table 2. After Fe^{3+} ions biosorption the FTIR spectra had some changes. The wave numbers at 3290 cm^{-1} and at 2921 cm^{-1}shifts to 3296 cm^{-1} and to 2929 cm^{-1} respectively. Also, the peaks at 1602 cm^{-1} shifts to 1616 cm^{-1} and at 1220 cm^{-1} changes to 1211 cm^{-1}. The peaks at 1028 cm^{-1} and at 815 cm^{-1} shifts to 1024 cm^{-1} and to 813 cm^{-1} respectively. Therefore, by comparing the wave numbers before and after Fe^{3+} ions biosorption, it suggested that the functional groups of carboxyl, hydroxyl and amide might contribute to the iron biosorption.

Table 2: FT-IR band and corresponding functional group

Peaks	Functional groups
3000 – 3500 cm^{-1}	-OH and -NH
2921 cm^{-1}	C-H
1602 cm^{-1}	Carboxyl group (-C = O)
1411 cm^{-1}	Symmetric C=O
1220 cm^{-1}	C–O stretch of COOH
1163 cm^{-1}	Symmetric $–SO_3$ stretching
1028 cm^{-1}	C–O (alcohol)
815 cm^{-1}	S=O stretching

SEM analysis at 500× and 1500× magnification was undertaken to find out the change in morphology after Fe^{3+} removal. The SEM images for the algae biomass *Sargassum Vulgare* before and after biosorption are shown in Fig.2. After metal binding, minor modifications are observed and the microstructures become deeper. The changes in the morphological are generally the result of the disruption of the cross-linking between the metal ions and negatively charged chemical groups e.g. carboxyl, hydroxyl groups in the cell wall. The brown algae contain a light metals such as sodium, magnesium and calcium, which probably creates on the surface an ion exchange with the Fe^{3+}, which might be caused alteration of the surface morphology [11,25].

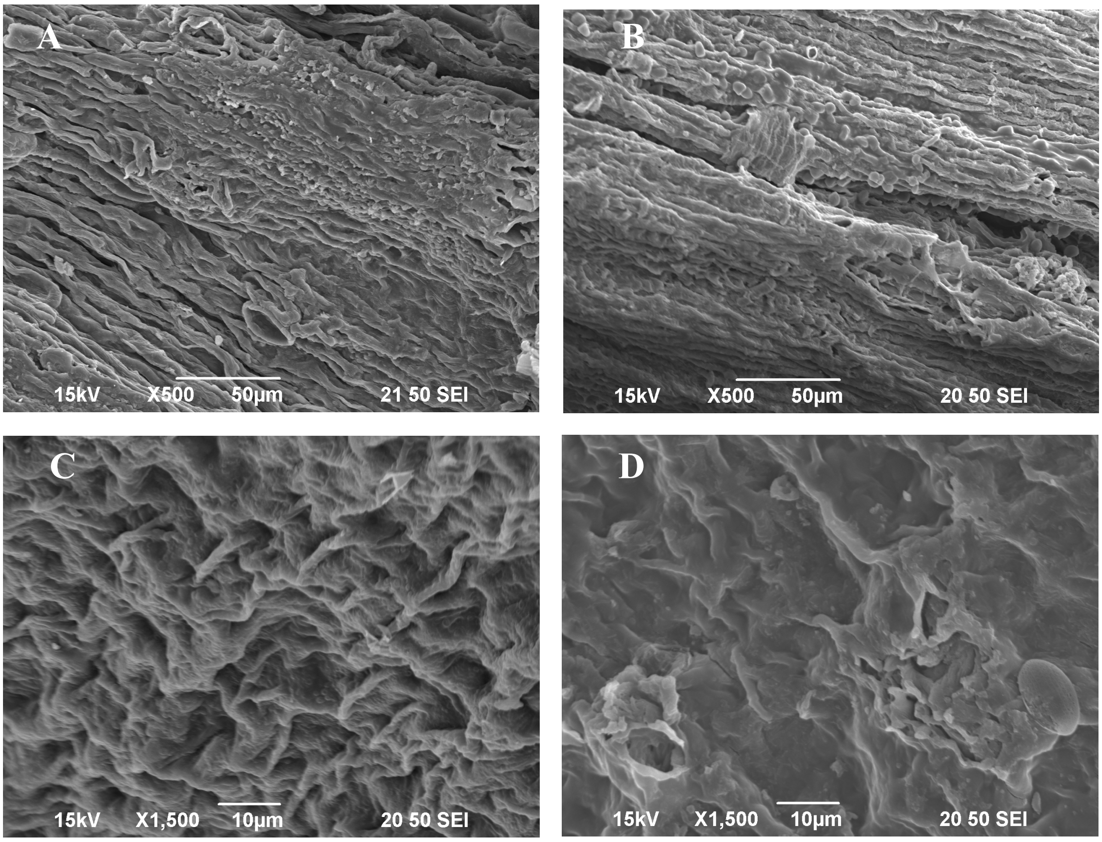

Figure 2: SEM of Raw Sargassum vulgare before iron elimination (A,C) and after iron removal (B,D)

3.2. Effect of pH

The effect of pH is one of the most important factors influencing the capacity of metal ion uptake by algal biomass. It is affects the surface properties of the biosorbent as well as the metal ion form in solution [26]. In our study, the effect of pH on Fe^{3+} biosorption was presented in Fig. 3. The biosorption capacity of Fe^{3+} increased up to pH= 2, then decreased at higher pH values. However, when pH was higher than 2, due to iron hydroxide precipitation, there is less amount of iron in solution available to be adsorbed onto the algae. The same results were obtained in literature [27]. Therefore, all others biosorption experiments were conducted at pH 2.

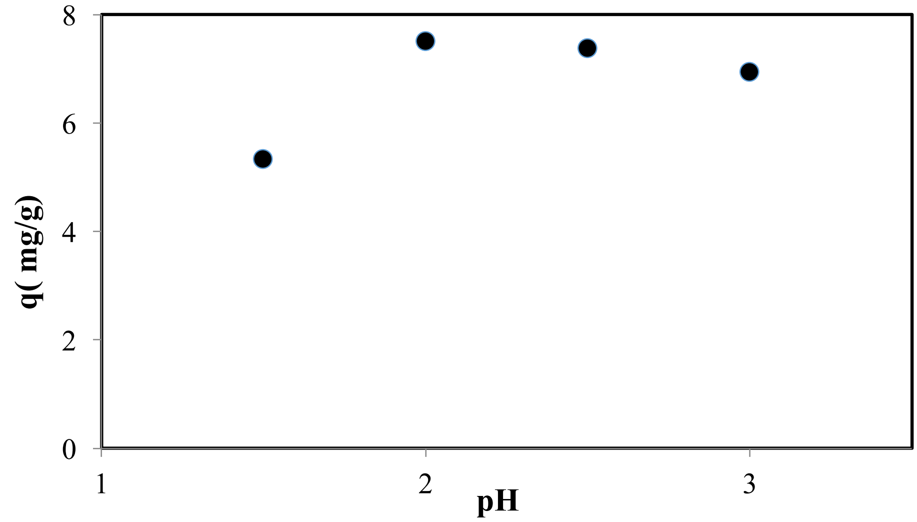

Figure 3: Effect of pH on Fe^{3+} biosorption using Sargassum Vulgare (stirring speed: 100rpm; contact time: 180 min; T: 298 K; Biomass dosage 5g/L .$[Fe^{3+}]$=50 mg /L)

3.3. Effect of contact time

Batch experiments were performed to find out the effect of contact time on Fe^{3+} biosorption. The interval time was ranging from 5 to 180 min and kept all others parameters constant. As shown in Fig.4, the uptake of Fe^{3+} onto algae biomass was enhanced with increasing the time up to 50 min, beyond it is became constant.

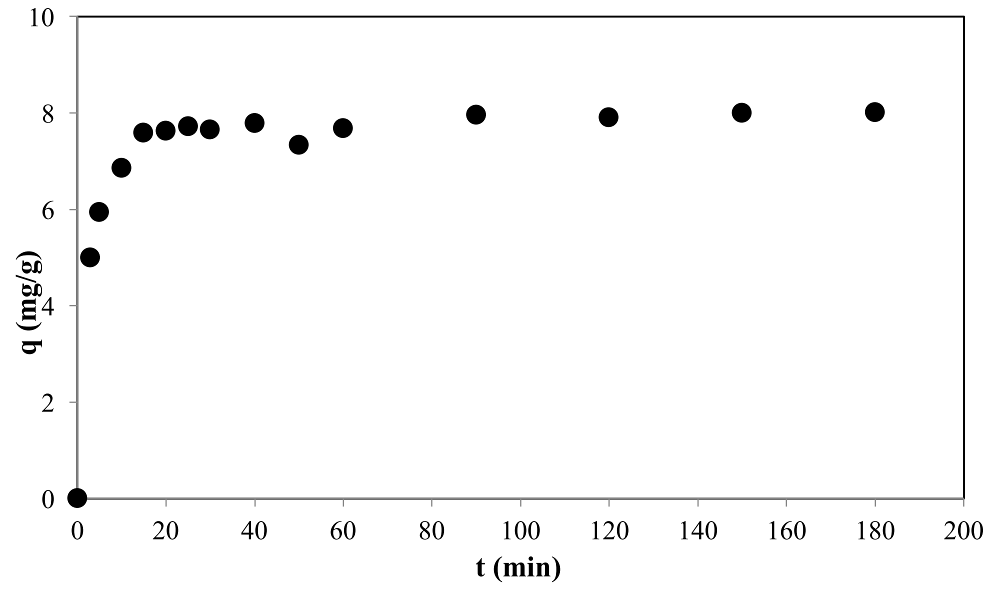

Figure 4: Effect of the contact time on Fe^{3+} biosorption using Sargassum Vulgare (Stirring speed 100 rpm; T 298 K, algae dosage 5 g /L, $[Fe^{3+}]$= 50 mg/L, pH =2)

The initial faster rate could be explained by the higher free surface available initially. Similar results are reported by other authors [28,29]. Therefore, a contact time of 120 min, was selected for all the equilibrium tests and the data obtained from this experiment were further used successfully to evaluate the kinetics of the biosorption process.

3.4. Effect of biosorbent dosage

The influence of algae biomass dosage on Fe3^{+} removal was evaluated by different biomass dosage ranging from 1 - 10 g /L. According to Fig 5, the removal efficiency increased to 76 % by increasing biomass dosage up to 5 g /L. However, there was only a slight change in the extent of iron biosorption, when the biosorbent dose was over 5 g/L. This trend could be explained as a consequence of partial aggregation of biomass at higher biomass concentration, which results in the decrease in effective surface area for the biosorption [24,30]. In the present work, the optimum biomass dosage was selected as 5 g/L for further experiments.

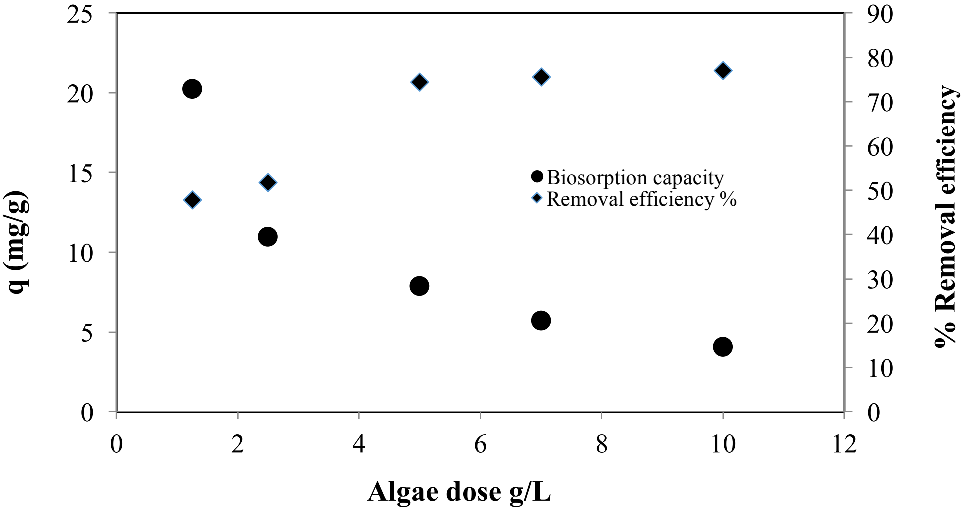

Figure 5: Effect of the biomass dosage on Fe3+ biosorption

3.5. Effect initial metal concentration

The influence of iron initial concentration was investigated at the suitable experimental conditions. The results are giving in Fig.6. The biosorption capacity of brown algae increases from 2.35 to 13.62 mg/g as the metal concentration increases from 25 to 100 mg/L. The higher metal ion concentration produce an enhanced number of attractive interaction between the solid and the aqueous phase [3,31].

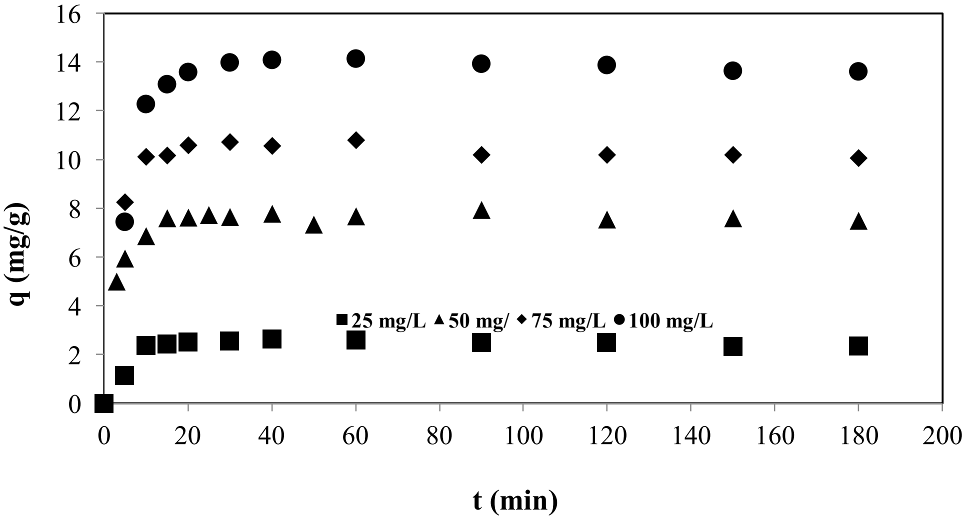

Figure 6: Influence of the different initial Fe^{3+}concentrations on the algae biosorption

3.6. Kinetic modeling

In order to analyze the biosorption kinetic of Fe^{3+} onto brown algae waste biomass, two kinetic models, pseudo first order and pseudo second order, were tested to fit the kinetic experimental data, and the nonlinear regression were performed to determine the model parameters (Fig.7 and 8).The results kinetic models parameters for different initial Fe3+ concentration are summarized in Table.3. The correlation coefficients R^2 and low RMSE values obtained for the pseudo- first-order kinetic model is indicative of the biosorption of Fe^{3+} onto *Sargassum* biomass follow the pseudo first order model [32,33].

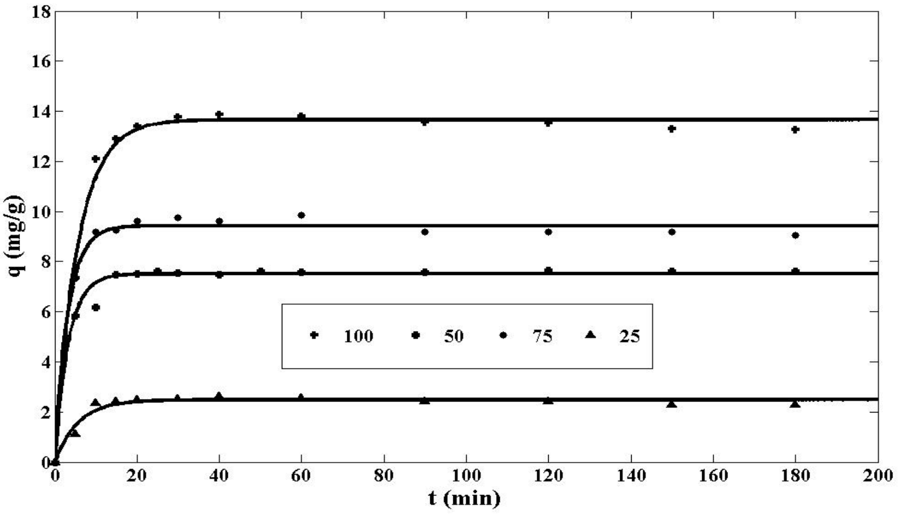

Figure 7: Pseudo first order model

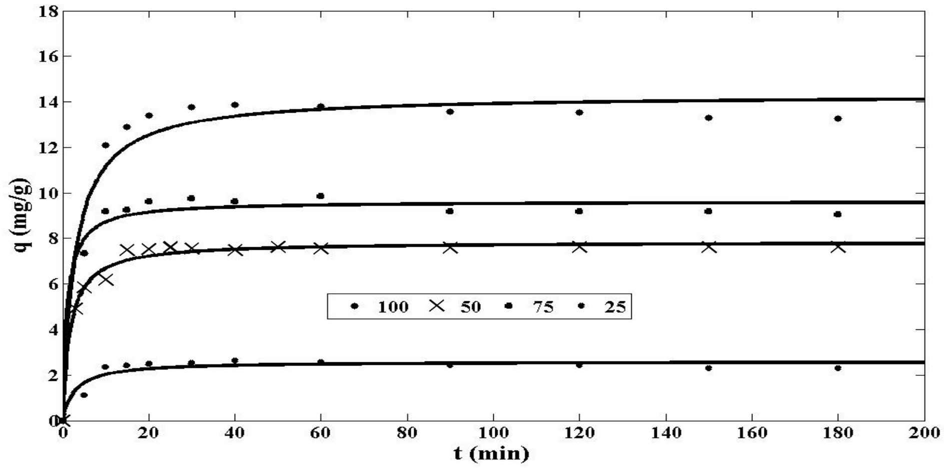

Figure 8: Pseudo second order model

Table 3: Kinetic models parameters

Kinetic models		Fe^{3+} concentration mg/L			
		100	75	50	25
Pseudo first-order	$K_{1\ (1/min)}$	0.1786	0.3073	0.3057	0.1758
	$q_{1(mg/g)}$	13.66	9.434	7.512	2.483
	R^2	0.992	0.9906	0.9788	0.9534
	RMSE	0.3841	0.2775	0.3059	0.1753
Pseudo second-order	$K_{2(g\ /mg/\ min)}$	0.00247	0.1001	0.07391	0.1366
	$q_{2(mg/g)}$	14.31	9.628	7.845	2.459
	R^2	0.958	0.9756	0.9875	0.8953
	RMSE	0.8828	0.4478	0.2348	0.2627

3.7. Equilibrium modeling

The experimental data were modeled by the nonlinear fitting of Langmuir and Freundlich isotherms using MATLAB software (Fig.9). All models parameters are given in Table 4. It is apparent that equilibrium data of biosorption onto brown algae are fitted well by the Langmuir isotherm, according the high of correlation coefficient R^2 (0.98), and a lower RMSE (0.539). Therefore, based on these results, the Langmuir model is considered the best model for describing the biosorption of Fe^{3+} onto Sargassum Vulgare. The same result was concluded for the biosorption of iron on crude olive stone [34] and on Rhizopus arrhizus biomass[35].

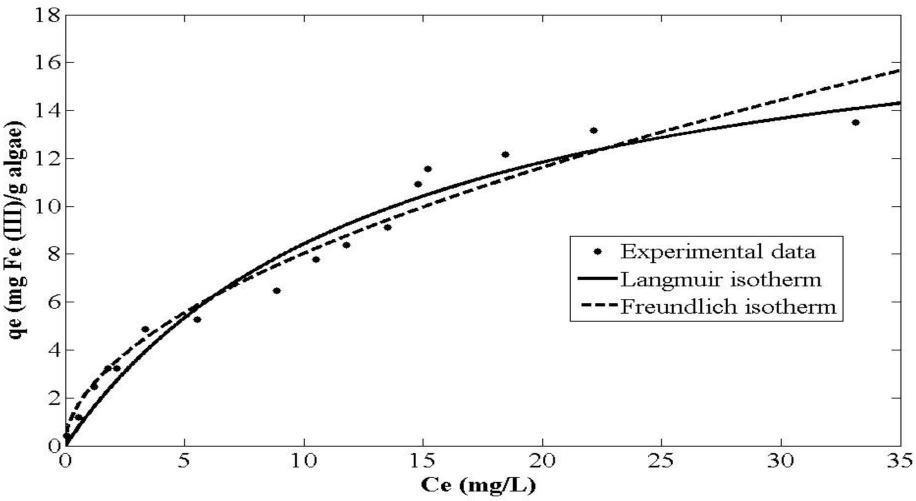

Figure 9: Langmuir and Freundlich isotherms of Fe^{3+} on algal biomass.

Table 4: Langmuir and Freundlish isotherm parameters

Langmuir isotherm				Freundlich isotherm			
$k_{L\ (L/mg)}$	$q_{m(mg/g)}$	R^2	RMSE	$k_{f(L/g)}$	n	R^2	RMSE
0.0736	19.86	0.9796	0.856	2.629	1.708	0.9555	1.457

3.8. Thermodynamic study

The value of the parameters (ΔG, ΔH, ΔS) obtained from plot of Ln k_D versus 1/T (Fig.10) are given in Table 5. All values for ΔG were negative, indicating the thermodynamic feasibility and spontaneous nature of the Fe^{3+} biosorption. The negative value of (ΔH) -23.24 kJ/mol, confirm that the biosorption of Fe^{3+} onto dried Sargassum Vulgare was an exothermic process. The negative entropy (ΔS) −0.079 kJ/mol/k, suggests a decrease in the randomness at the solid/solution interface during the biosorption of Fe^{3+} onto *Sargassum Vulgare* [33,36,37].

Table 5: Thermodynamic parameters

Temperature (k)	ΔG (kJ / mol)	ΔH(kJ / mol)	ΔS (kJ/mol/k)
298	-5.69	-23.24	-0.079
308	-4.26		
318	-3.16		

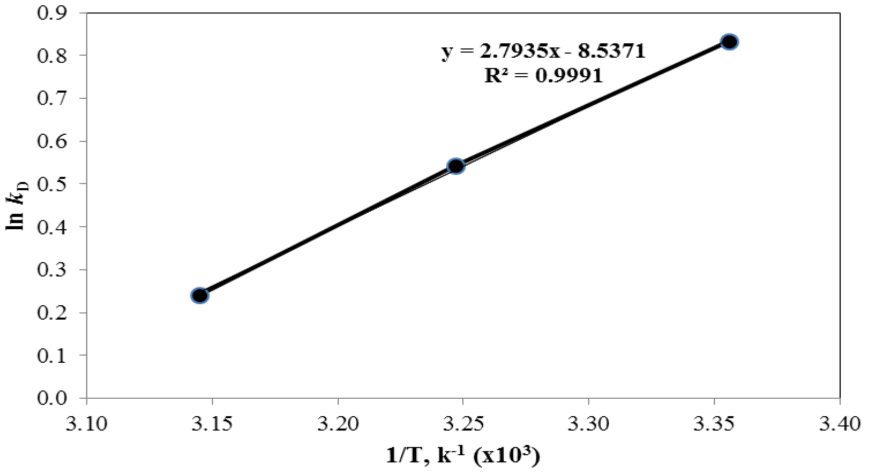

Figure 10: Plot of Ln k_D vs. 1/T for the estimation of thermodynamic parameters for biosorption of Fe3+ onto Sargassum Vulgare

3.9. Desorption and regeneration

Desorption studies of iron loaded by algae biomass in 0.001 EDTA, 0.1 HCl and 0.1 HNO_3 solutions revealed that more than 90 % of the adsorbed iron was desorbed from the algal biomass in the first cycle. According to Table 6, the reusability of the biosorbent, adsorption- desorption cycle of iron was repeated three times, and EDTA solution exhibited a better regeneration performance for Fe^{3+} than other reagents. The same results are reached in [37–39].

Table 6: Influence of different desorbents solutions on Fe^{3+} on raw alga

Cycle	Amount of Fe^{3+} recovered (%)		
	0.001 M EDTA	0.1 M HCl	0.1 M HNO_3
1	94.43	86.86	79.58
2	88.86	68.90	71.79
3	53.93	23.33	51.85

Conclusion

The brown macroalgae *Sargassum Vulgare* was tested for the biosorption of Fe^{3+} in batch system at pH 2. From the FTIR analysis, it was observed that the high adsorption capacity of the adsorbent is due to the presence of different surface functional groups such as carboxyl and amine groups. Various biosorption parameters were investigated in this study. Two kinetic models Pseudo-I- order and pseudo-II-order were used to fitting the experimental data, the biosorption process followed the first order model with correlation coefficient R^2 about 0.99. The isotherm sorption was fitted better by Langmuir model with q_m= 19. 86 mg Fe^{3+}/g biomass and R^2= *0.97.* The thermodynamic parameters ΔH, ΔS and ΔG were calculated. The result showed an exothermic biosorption. The desorption study reveal that among different desorbing solutions, the EDTA show the best results for recovering Iron metal from algae biosorbent with three cycles biosorption-desorption.

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References

1. Abdi O, Kazemi M. A review study of biosorption of heavy metals and comparison between different biosorbents. *J Mater Environ Sci*.6(2015) 1386-1399.
2. Farooq U, Kozinski JA, Khan MA, Athar M. Biosorption of heavy metal ions using wheat based biosorbents - A review of the recent literature. *Bioresour Technol*.101 (2010) 5043-5053.
3. Zeraatkar AK, Ahmadzadeh H, Talebi AF, Moheimani NR, McHenry MP. Potential use of algae for heavy metal bioremediation, a critical review. *J Environ Manage*. (2016) 181.
4. Papanikolaou G, Pantopoulos K. Iron metabolism and toxicity. *Toxicol Appl Pharmacol*. 202 (2005) 199-211
5. Reddy DHK, Lee SM. Water Pollution and Treatment Technologies. *J Env Anal Toxicol*. 2(2012):5-6.
6. Kirkelund GM, Magro C, Guedes P, Jensen PE, Ribeiro AB, Ottosen LM. Electrodialytic removal of heavy metals and chloride from municipal solid waste incineration fly ash and air pollution control residue in suspension - Test of a new two compartment experimental cell. *Electrochim Acta*. 181 (2015) 73-81.
7. Kanamadi RD. Biosorption of Heavy Metals. 7 (2003).
8. Fomina M, Gadd GM. Biosorption: Current perspectives on concept, definition and application. *Bioresour Technol*. 160 (2014) 3-14.
9. Sheng PX, Tan LH, Chen JP, Ting Y. Biosorption Performance of Two Brown Marine Algae for Removal of Chromium and Cadmium. *J Dispers Sci Technol*. 25(2005) 679-686.
10. Slimani Alaoui N, El Laghdach A, Cuerda Correa E. Manuel EM, Stitou M, El Yousfi F, Jbari N. Preparation of bone chars by calcination in traditional furnace. *J Mater Environ Sci*. 5(2014) 476-483.
11. He J, Chen JP. A comprehensive review on biosorption of heavy metals by algal biomass: materials, performances, chemistry, and modeling simulation tools. *Bioresour Technol*. 160 (2014) 67-78.
12. Davis T a, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res*. 37 (2003) 4311-4330.
13. Hansen HK, Gutiérrez C, Madrid A, Jimenez R, Larach H. Possible Use of the Algae Lessonia nigrescens as a Biosorbent: Differences in Copper Sorption Behavior Using Either Blades or Stipes. *Waste and Biomass Valorization*. (2016).
14. Masood F, Malik A. Biosorption of metal ions from aqueous solution and tannery effluent by *Bacillus* sp.

FM1. *J Environ Sci Heal Part A*. 46 (2011) 1667-1674.

15. Karthikeyan S, Balasubramanian R, Iyer CSP. Evaluation of the marine algae Ulva fasciata and Sargassum sp. for the biosorption of Cu(II) from aqueous solutions. *Bioresour Technol*. 98 (2007) 452-455.
16. Lou Z, Wang J, Jin X, et al. Brown algae based new sorption material for fractional recovery of molybdenum and rhenium from wastewater. *Chem Eng J*. 273 (2015) 231-239.
17. Aravindhan R, Rao JR, Nair BU. Kinetic and equilibrium studies on biosorption of basic blue dye by green macro algae Caulerpa scalpelliformis. *J Environ Sci Health A Tox Hazard Subst Environ Eng*. 42 (2007) 621-631.
18. Ortiz C, Pizarro J, Barros D, Castillo X, Giraldo L, Carlos J. Characterization of copper (II) biosorption by brown algae Durvillaea antarctica dead biomass. (2015) 645-658.
19. Kabbaj H, El Mai H, Riãnao MDG, Stitou M. Physicochemical characterization and analysis of total metal concentration of grease and wastewater samples: Case study for two wastewater treatment plants in the North of Morocco: Tangier and Tetouan. *J Mater Environ Sci*. 5 (2014) 1622-1632.
20. Davis TA, Volesky B, Vieira RHSF. Sargassum seaweed as biosorbent for heavy metals. *Water Res*. 34 (2000) 4270-7278.
21. Ho YS, McKay G. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Saf Environ Prot*.76 (1998) 332-340.
22. Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochem*.34 (1999) 451-465.
23. Hasan SH, Srivastava P. Batch and continuous biosorption of Cu2+ by immobilized biomass of Arthrobacter sp. *J Environ Manage*. 90 (2009) 3313-3321.
24. Daneshvar E, Kousha M, Sohrabi MS, Khataee A, Converti A. Biosorption of three acid dyes by the brown macroalga Stoechospermum marginatum: Isotherm, kinetic and thermodynamic studies. *Chem Eng J*.195-196 (2012) 297-306.
25. Yang L, Chen JP. Biosorption of hexavalent chromium onto raw and chemically modified Sargassum sp. *Bioresour Technol*. 99 (2008) 297-307.
26. Plazinski W. Binding of heavy metals by algal biosorbents. Theoretical models of kinetics, equilibria and thermodynamics. *Adv Colloid Interface Sci*. (2013) 197-198.
27. Ghimire KN, Inoue K, Ohto K, Hayashida T. Adsorption study of metal ions onto crosslinked seaweed Laminaria japonica. *Bioresour Technol*. 99 (2008) 32-37.
28. Mishra A, Tripathi BD, Rai AK. Biosorption of Cr(VI) and Ni(II) onto Hydrilla verticillata dried biomass. *Ecol Eng*. 73 (2014) 713-723.
29. Bulgariu D, Bulgariu L. Equilibrium and kinetics studies of heavy metal ions biosorption on green algae waste biomass. *Bioresour Technol*. 103 (2012) 489-493.
30. Gupta VK, Rastogi A, Nayak A. Biosorption of nickel onto treated alga (Oedogonium hatei): Application of isotherm and kinetic models. *J Colloid Interface Sci*. 342 (2010):533-539.
31. Baral SS, Das N, Roy Chaudhury G, Das SN. A preliminary study on the adsorptive removal of Cr(VI) using seaweed, Hydrilla verticillata. *J Hazard Mater*. 171 (2009) 358-369.
32. Liu Y, Cao Q, Luo F, Chen J. Biosorption of Cd2+, Cu2+, Ni2+ and Zn2+ ions from aqueous solutions by pretreated biomass of brown algae. *J Hazard Mater*. 163(2009) 931-938.
33. Hodaifa G, Alami SBD, Ochando-Pulido JM, Victor-Ortega MD. Iron removal from liquid effluents by olive stones on adsorption column: Breakthrough curves. *Ecol Eng*. 73 (2014) 270-275.
34. Nieto LM, Alami SBD, Hodaifa G, et al. Adsorption of iron on crude olive stones. *Ind Crops Prod*. 32 (2010) 467-471.
35. Sağ Y, Kutsal T. The simultaneous biosorption of Cr(VI), Fe(III) and Cu(II) on Rhizopus arrhizus. *Process Biochem*. 33 (1998) 571-579.
36. Tan C yun, Li M, Lin YM, Lu XQ, Chen Z liang. Biosorption of Basic Orange from aqueous solution onto dried A. filiculoides biomass: Equilibrium, kinetic and FTIR studies. *Desalination*. 266 (2011) 56-62.
37. Gupta VK, Rastogi A. Biosorption of hexavalent chromium by raw and acid-treated green alga Oedogonium hatei from aqueous solutions. *J Hazard Mater*. 163 (2009) 396-402.
38. Beolchini F, Pagnanelli F, Toro L, Vegliò F. Biosorption of copper by Sphaerotilus natans immobilised in polysulfone matrix: Equilibrium and kinetic analysis. *Hydrometallurgy*.70 (2003) 101-112.
39. Das N. Recovery of precious metals through biosorption - A review. *Hydrometallurgy*. 103 (2010) 180-89.

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