Kinetics, Equilibrium, and Thermodynamic Studies on Fe^{3+} Removal from Aqueous Solutions by Chemically Modified Brown Algae

Benaisa, Souad

Laboratoire de l'Eau, d'Études et d'Analyses Environnementales, Faculté des Sciences,
Université Abdelmalek Essâadi, Tétouan, MOROCCO

Arhoun, Brahim; Villen-Guzman, María

Chemical Engineering Department, Faculty of Sciences, University of Malaga, 29071 Malaga, SPAIN

El Mail, Rachad

Laboratoire de l'Eau, d'Études et d'Analyses Environnementales, Faculté des Sciences,
Université Abdelmalek Essâadi, Tétouan, MOROCCO

Gomez-Lahoz, Cesar*+; Rodriguez-Maroto, José M.

Chemical Engineering Department, Faculty of Sciences, University of Malaga, 29071 Malaga, SPAIN

ABSTRACT: *Sargassum Vulgare was used as an effective biosorbent for the removal of Fe^{3+} from aqueous solutions. Results for batch operation are presented for biosorption onto algal biomass, raw and modified with HNO_3, HCl, NaCl, and $CaCl_2$. NaCl was selected as the best modifier for the algae surface for the improvement of the sorption capacity. Optimum biosorption conditions were determined as a function of contact time, biomass dosage, initial metal concentration, and temperature. The Langmuir isotherm yields high regression values for a maximum monolayer sorption capacity of the modified biomass of 30.52 mg/g at optimum conditions (pH = 2, dose = 5 g/L, t = 120 min, and T= 298 K). This represents an increase of more than 50 % concerning the raw algae. The kinetics of sorption followed the pseudo-first-order rate equations and is fast enough to prove the technique feasible. The thermodynamic parameters showed that the adsorption of Fe^{3+} using algal biomass was feasible, spontaneous, and exothermic. Modified algae could be regenerated once using 0.001M EDTA solution, and a recovery of 90% of Fe^{3+} was obtained. Fourier Transform InfraRed (FT-IR) spectroscopy and Scanning Electron Microscopy (SEM) were used to characterize the surface of modified algae.*

KEYWORDS: *Biosorption; Brown algae; Chemical modification; Fe^{3+}, Kinetic models; FT-IR.*

INTRODUCTION

The use of heavy metals in several industries, such as plating facilities, mining operations, fertilizers, tanneries, batteries, paper, and pesticide industries, involves wastewater pollution, and research for pollution removal techniques is required [1,2]. Heavy metals are not degradable and pose a very important threat to the environment, health, and living organisms [3-5] if introduced into the food chain. However, several methods are used for metal removal from wastewater including chemical precipitation, ion exchange using synthetic membranes, and electro-dialysis, which may be expensive or ineffective [6].

In addition to the mentioned techniques, there is a wide variety of sorption materials that may be used for the removal of contaminants [7–11]. Biosorption of heavy metals on renewable materials could be a more effective method, presenting a good performance, minimization of chemical/biological sludge generation, and the use of low-cost biomass [6,12,13]. The use of brown algae has been considered as a potential biosorbent due to the presence of various biochemical compounds on the cell wall surface such as fucoidan and alginate, which can act as binding sites for metals [4,5,14,15]. This biosorption capacity can be increased by the surface modification of the biomass after treatment with some chemicals. In the literature, various chemical modifiers of the surface, such as acids, alkalis, and organic chemicals have been investigated with important improvements in the metal removal capacity [16,17].

Iron is one of the most used metals in industrial production because of its low price and physical properties. Even if it is not among the most hazardous metals, at high concentrations may cause serious problems in aqueous streams [18–20]. The presence of iron in wastewater has been associated with industrial sources, such as mining, the iron and steel industry, and metal corrosion. In addition, iron in drinking water affects important properties such as taste, color, and turbidity [21-23]. Various studies have been focused on the removal of Fe^{3+} using different biomass sources such as green tomato husk [24], crude olive stones [25], pre-treated orange peel [26], E. coli biofilm supported on kaolin [27], bacterial dead [28], and microalgae of *Scenedesmus obliquus* [29]. To the best of the authors' knowledge, there is no previous research on the use of brown macro-alga as a biosorbent for Fe^{3+} removal.

In general, industries generate an enormous quantity of wastewater containing various concentrations of Fe^{3+} together with other heavy metals such as Cu, Zn, Cd, and Cr [30–32]. For this reason, in previous work, we presented results for the biosorption of Fe^{3+} from an aqueous solution using raw brown algae *Sargassum Vulgare* [33]. In this work, results for the influence of the surface modification of the same algae, using acid and alkali chemicals, are presented.

The influence on the Fe^{3+} biosorption efficiency of different parameters is determined including contact time, biomass dosage, initial metal concentration, and temperature. Results for the biosorption kinetics are also presented. The biosorption equilibrium isotherm is studied using Langmuir, Freundlich, Redlich-Peterson, Slips, and Toth equations. The surface of the modified algae is also explored using Fourier Transform InfraRed (FT-IR) spectroscopy and Scanning Electron Microscopy (SEM). Also, results for the regeneration of the biosorbent are presented.

EXPERIMENTAL SECTION

Preparation of biosorbent and iron solutions

The brown algae *Sargassum Vulgare* collected from the northern coast of Morocco, was washed several times with deionized water and sun-dried for 24 h and then oven-dried at 60°C overnight. The obtained biomass was crushed and sieved to $0.2 < \varnothing < 0.75$ mm. The solutions selected for the surface modification study were 0.1 M of HNO_3, HCl, NaCl, and $CaCl_2$. In each case, 1 g of dry biomass was suspended in 100 mL of solution and stirred at 130 rpm at 25 °C for 24 h. The collected samples were washed with distilled water and oven dried at 60 ºC for 24 h.

Aqueous solutions of Fe^{3+} were prepared by dissolving the required quantity of $(NH_4)Fe(SO_4)_2 12H_2O$ in deionized water. The pH value of the solutions at pH= 2 was adjusted using 0.1 M solutions of H_2SO_4 or NaOH.

Batch biosorption

The biosorption studies to explore the effects of the surface modifiers were carried out in glass bottles containing 100 mL of the Fe^{3+} solution and 5 g/L of algae at 25 °C under continuous stirring at 130 rpm. The effect of contact time was studied within the range between 5 to 180 minutes using 50 mg/L solutions of Fe^{3+} at a pH value of 2 [34].

The effect of algae dose was studied ranging from 1 to 10 g/L for the surface modifier with the best removal efficiency. To determine the equilibrium isotherms at 25 °C, experiments were performed with the initial Fe^{3+} concentration from 5 to 100 mg/L and a contact time of 120 min. To study the thermodynamics of Fe^{3+} biosorption on modified algae, the effect of temperature was also investigated at 298, 308, and 318 K, for the optimal conditions (pH=2, algae dosage 5 g/L, $[Fe^{3+}]$=50 mg/L and contact time 120 min)

The biomass concentration of the adsorbed Fe^{3+} and the percent of metal removal was calculated using the following equations:

$$q = \frac{C_i - C_f}{m} \times V \qquad (1)$$

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \qquad (2)$$

Where q (mg/g) is the biomass phase concentration after equilibrium, C_i and C_f are respectively the initial and equilibrium aqueous concentrations (mg/L) of Fe^{3+}, m is the mass (g) of dry biosorbent suspended in the solution and V is the volume of the aqueous solution.

The difference between the biosorption of the raw and the modified biosorbent was obtained as:

$$\Delta q_e = \frac{(q_{e2} - q_{e1})}{q_{e1}} \times 100 \qquad (3)$$

Where q_{e1} (mg/g) and q_{e2} (mg/g) are the biomass concentrations of metal ions on the raw and modified biomass at equilibrium, respectively.

For the desorption study, 0.5 g of the surface-modified biomass was contacted with 100 mL of Fe^{3+} solution (50 mg/L). After the biosorption experiment, the biomass was collected and washed with deionized water to remove the metal ions present in the aqueous phase. Then, it was transferred to 100 mL of adsorbent solutions (0.1M HCl, 0.1M HNO₃, or 0.001M EDTA). The mixtures were shaken for 120 min at optimal conditions. The desorption percentage was calculated according to the following equation [35]:

$$\% \text{ Desorption} = \frac{C_D V_D}{q_e m} \times 100 \qquad (4)$$

Where C_D is the metal concentration in the aqueous solution at the end of the experiment, V_D is the volume of eluent used for desorption and m is the mass of biomass,

q_e is the initial concentration of the biomass before the desorption experiment.

The samples were analyzed to determine the residual concentrations of Fe^{3+} using Varian SpectrAA 110 Atomic Absorption Spectrometer (AAS). Each experiment was duplicated to obtain the mean values.

Characterization

The sorption process of cations between the aqueous and the biomass phases is probably a combination of several processes with a main contribution, probably, of the ion exchange processes. The BET surface for the raw algae is 0.1265 m^2/g. We don't expect that the pretreatments will introduce any significant change in this small specific surface. Also, a conventional assay was performed with the raw algae for the determination of the zero-charge point, which was determined to be at pH = 5.2.

The functional groups of the raw biomass (a), pre-treated algae before (b), and after (c) Fe^{3+} biosorption were obtained using Fourier Transform InfraRed (Bruker Vertex 70 FT-IR spectrophotometer). The surface morphology was examined on a JSM-840 Scanning Electron Microscope (JEOL, United States).

Kinetic modeling

In order to evaluate the kinetics of Fe^{3+} biosorption on modified brown algae *Sargassum Vulgare,* the experimental data were analyzed using the pseudo-first order and pseudo-second order equations.

The pseudo-first-order kinetic model of Lagergren is given as

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad (5)$$

Where q_t (mg/g) is the amount of biosorbed metal at time t (min) and k_1 (min⁻¹) is the rate constant of the pseudo-first-order kinetic model

The pseudo-second-order process can be described as follows:

$$q_t = \frac{q_e^2 k_2 t}{1 + (q_e k_2 t)} \qquad (6)$$

Where q_e (mg/g) is the amount of biosorbed metal on the biomass at equilibrium and k_2 (g/mg.min) is the rate constant of the pseudo-second-order kinetic model.

Isotherm modeling

The values of the parameters of the Langmuir and Freundlich isotherms were fitted to the biosorption equilibrium results. The Langmuir model describes monolayer biosorption. It is expressed as follows [36]:

$$q_e = \frac{q_m(k_L C_e)}{1 + (k_L C_e)} \qquad (7)$$

where q_m (mg/g) is the saturated monolayer biosorption concentration capacity, k_L (L/mg) is the biosorption equilibrium constant and C_e (mg/L) is the metal equilibrium concentration in the aqueous phase.

The Freundlich isotherm can be expressed by the equation

$$q_e = k_f C_e^{1/n} \qquad (8)$$

where k_f is the Freundlich biosorption constant related to the biosorption concentration and n is a dimensionless parameter associated with the adsorption intensity.

We have tested also the Redelich-Peterson (eq. 9), Sips (Eq. (10)), and Toth (Eq. (1)) isotherms; all of them use three parameters and the equations are as follows:

$$q_e = \frac{k_{RP} C_e}{1 + a_{RP} C_e^{\beta_{RP}}} \qquad (9)$$

Where k_{RP} is the Redlich-Peterson model isotherm constant, a_{RP} is the Redlich-Peterson model constant and β_{RP} is the Redlich-Peterson model exponent.

$$q_e = \frac{k_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \qquad (10)$$

Where k_S is the Sips model isotherm constant; a_S is the Sips model constant and β_S is the Sips model exponent.

$$q_e = \frac{q_{max} b_T C_e}{\left[1 + (b_T C_e)^{\frac{1}{n_T}}\right]^{n_T}} \qquad (11)$$

Where q_{max} is the maximum metal sorption, b_T is the Toth model constant and n_T is the Toth model exponent.

Evaluation of model performance

The parameter values of the model were fitted using Solver in MS Excel. The coefficient of determination (R^2) and the residual Root Mean Square Error (RMSE) values were used to evaluate the accuracy of models [37].

$$R^2 = \qquad (12)$$
$$\frac{\sum_{i=1}^{N}(q_{e,model} - \bar{q}_{e,exp})^2}{\sum_{i=1}^{N}\left[(q_{e,model} - \bar{q}_{e,exp})^2 + (q_{e,model} - q_{e,exp})^2\right]}$$

$$RMSE = \sqrt{\frac{1}{N-p}\sum_{I=1}^{N}(q_{e,exp} - q_{e,model})_i^2} \qquad (13)$$

Where $q_{e,exp}$ (mg/g) is the experimental sorption concentration, $\bar{q}_{e,exp}$ (mg/g) is the average experimental sorption concentration, $q_{e,model}$ (mg/g) is the sorption concentration estimated by the model, N is the number of observations in the experimental design, and p is the number of parameters to be determined. An indication of a good fit would yield an R^2 value close to 1 and a value of RMSE close to zero.

Biosorption thermodynamics

The equilibrium thermodynamics was studied from the variations of the experimental results at different temperatures. Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were determined using the following equations:

$$\Delta G^0 = -RT \ln k_D \qquad (14)$$

where R is the universal gas constant (8.314 J/mol.K), T (K) is the temperature and k_D is the distribution coefficient (dimensionless). The entropy, ΔS^0, and the enthalpy ΔH^0 can be obtained from the slope and intercept of a Van't Hoff plot of Ln k_D versus $1/T$.

$$\ln k_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (15)$$

RESULTS AND DISCUSSION
Influence of biomass modification and contact time

Results for the Fe^{3+} biosorption onto raw and pre-treated algae (0.1 M solutions of $CaCl_2$, NaCl, HCl, and HNO_3) are presented in Fig. 1. As can be seen, the performance of the biosorbent decreased in the following order of the pre-treatment agent:

NaCl > $CaCl_2$ > raw biomass > HCl > HNO_3. Thus, the biomass modified with the NaCl solutions showed a biosorption increased concentration of about 20 % as compared with the raw biomass.

Results presented in Fig. 1 also indicate that, for the experimental conditions, almost all the Fe^{3+} sorption takes

place during the first 30 minutes and that 120 minutes are enough to consider that equilibrium has been reached.

It is generally assumed that the main sorption process is ion exchange. Therefore, it can be expected that as the charge of the cation increases and its size decreases, the higher the cation's tendency to be retained by the biomass. As a consequence, it could be expected that the biomass pre-treated with Na^+ will have the highest affinity for Fe^{3+}. Regarding the results obtained for the two acids, the biomass may undergo permanent modifications in the surface groups with a negative charge, and these changes are more significant for the nitric acid. In this case, a permanent loss of the total exchange capacity would take place [38-40].

Influence of algae dosage

As one increases the amount of biosorbent added to a certain volume of an aqueous solution, more binding sites are available for each cation in the solution. Thus, as can be seen in Fig. 2, the relative removal of Fe^{3+} increases as the biomass dosage increases. On the other hand, as the biomass dosage increases, the total amount of cations different from Fe^{3+} present in the aqueous-biomass system increases too, since they are incorporated mainly with the biomass. Therefore, it is also expectable that as the equilibrium Fe^{3+} concentration in the aqueous phase decreases, the other cations compete better for the binding positions. As a consequence, when the biomass dosage exceeds 5 g/L, for which the removal efficiency is 73 %, only marginal removal increases can be obtained [17].

Influence of initial Fe^{3+} concentration

Fig. 3 presents the results for the biosorption onto NaCl-modified algae for different initial Fe^{3+} concentrations versus time. As was observed in Fig. 1, for the experimental conditions the sorption process is relatively fast, with most of the retention taking place during the first 15 minutes. It can also be observed that as the initial aqueous phase, Fe^{3+} concentration increases the equilibrium biomass concentration increases, as expected. Also as expected, the slope of the metal uptake during the initial stages increases with the initial metal concentration [41].

Biosorption kinetics

Fig. 4 presents the results obtained for the kinetic models best fit the experimental values, whereas Table 1
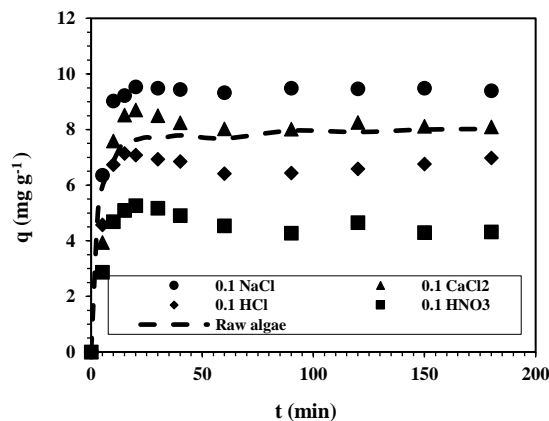

Fig. 1: Effect of the use of pre-treated algae on Fe^{3+} biosorption. (pH=2, algae dosage = 5g/L, [Fe^{3+}]$_0$=50 mg/L, T= 298 K).
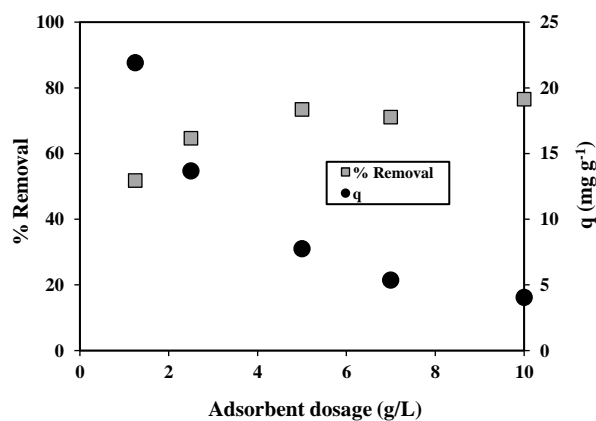

Fig. 2: Effect of NaCl modified-algae dosage on the removal of Fe^{3+} ([Fe^{3+}] = 50 mg/L, pH= 2, T= 298 K , t =120 min).
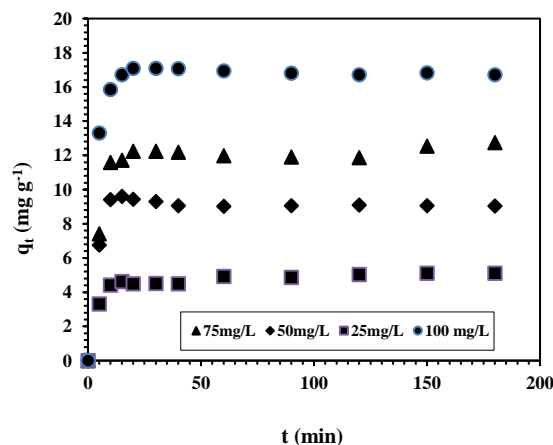

Fig. 3. Influence of different initial Fe^{3+} concentrations (pH= 2, NaCl modified-algae dosage = 5g/L).

Table 1: Kinetic models parameters.

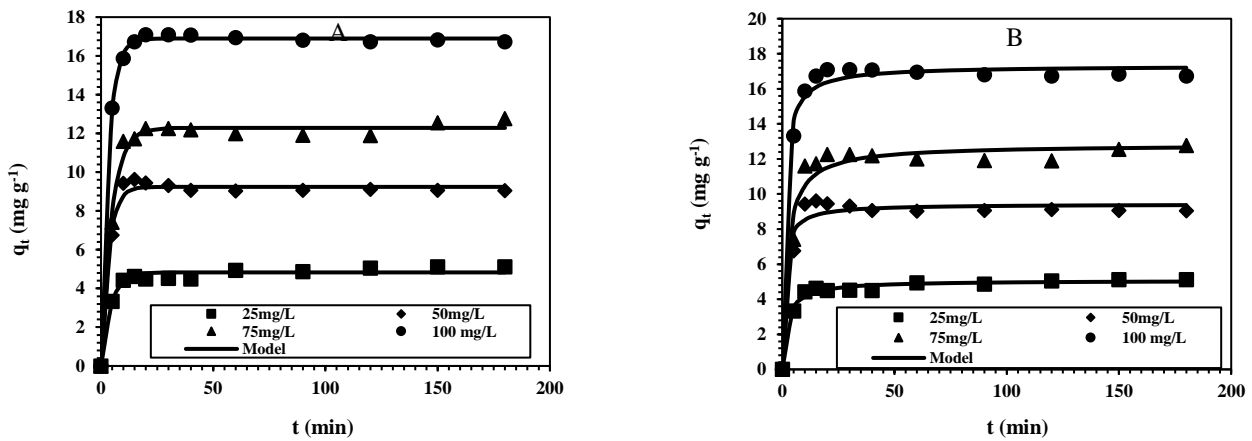| Kinetic models		Fe^{3+} concentration mg/L			
		25	50	75	100
Pseudo first-order	K_1 (1 min^{-1})	0.231	0.296	0.210	0.305
	q_1 (mg/g)	4.828	9.241	12.284	16.896
	R^2	0.9916	0.9965	0.9907	0.9974
	RMSE	0.1028	0.1691	0.3859	0.2147
Pseudo second-order	K_2 (g mg^{-1} min^{-1})	0.087	0.099	0.034	0.050
	q_2 (mg/g)	5.071	9.424	12.810	17.313
	R^2	0.9759	0.9750	0.9632	0.9868
	RMSE	0.1742	0.4521	0.770	0.5453

Fig. 4: Kinetic studies of Fe^{3+} biosorption onto NaCl -modified algae A) Pseudo-first-order model and B) Pseudo-second-order model (pH= 2, Algae dosage = 5 g/L).

summarizes the fitting results. As can be seen, the pseudo-first-order model yields the best results, according to the values of R^2, *RMSE*, and also the q_e value, which is closer to the experimental equilibrium value. These results also indicate that, for the experimental conditions, the sorption process is fast enough to be technically feasible.
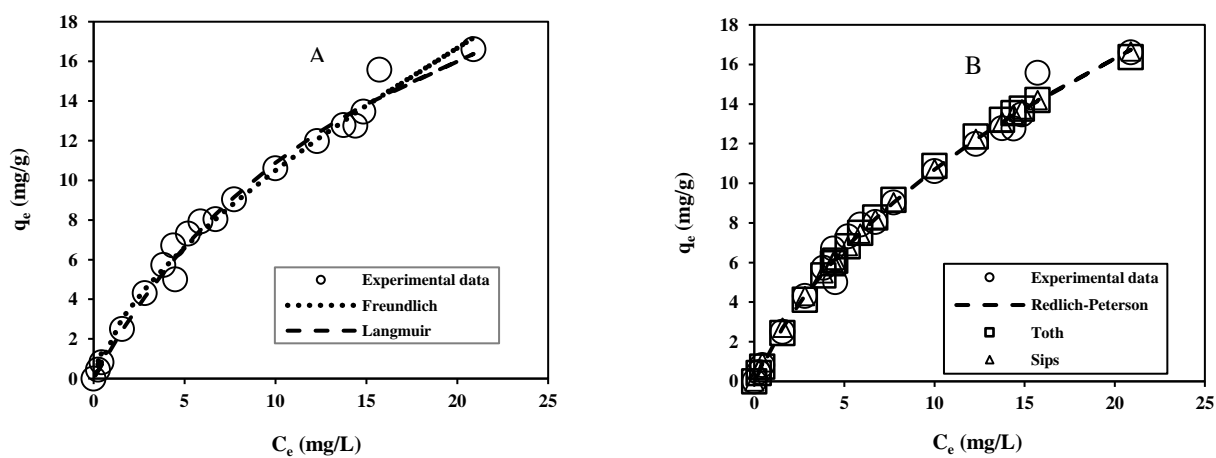
Biosorption isotherm

Fig. 5 presents the equilibrium results for different Fe^{3+} concentrations on the NaCl-modified algae biomass and in the aqueous phase at 25 °C. Fig. 5A also presents the results for the best fit obtained for the Freundlich and Langmuir isotherms, whereas the results for the Redlich-Peterson, Toth, and Slips isotherms are presented in Fig. 5B. The values for the parameters for the five isotherms are presented in Table 2, together with the R^2 and *RMSE*

values. As can be seen, the R^2 and RMSE values range respectively from 0.9870 and 0.6056 for the Freundlich isotherm to 0.9893 and 0.5563 for Redlich-Peterson. Thus, there is little difference between the statistical values obtained for the five isotherms, and all of them yield a good agreement with the experimental results. Consequently, we have chosen the Langmuir isotherm for the interpretation of the results, since this isotherm is simple enough, because involves only two parameters, and is derived from mass-action kinetics where the reaction is the chemisorption process and sorption takes place as a monolayer onto the solid surface, allowing the thermodynamic interpretation of the results. The maximum biosorption capacity, as obtained from the Langmuir isotherm, of Fe^{3+} for the NaCl-modified algae (30.52 mg/g) is higher than the value obtained previously [33] using raw

Table 2: Isotherms parameters.

Model	Parameters	Value
Langmuir	k_L (L / mg)	0.055
	q_m (mg/g)	30.524
	R^2	0.9886
	RMSE	0.5826
Freundlich	k_f (L/g)	2.249
	n	1.495
	R^2	0.9870
	RMSE	0.6056
Redlich-Peterson	K_{RP} (L/g)	2.303
	a_{RP} (L/mg)	0.251
	β_{RP}	0.661
	R^2	0.9893
	RMSE	0.5563
Sips	K_S (L/g)	1.963
	a_S (L/mg)	0.044
	β_S	0.856
	R^2	0.9890
	RMSE	0.5614
Toth	q_{max} (mg/g)	30.524
	b_T	0.055
	n_T	0.339
	R^2	0.9885
	RMSE	0.5826

Fig. 5: Biosorption isotherms of Fe^{3+} onto NaCl-modified algae A) two-parameters isotherms and B) three-parameters isotherms.

algae (19.86 mg/g) indicating that the pre-treatment modification allows an improvement of about 54 %.

FT-IR analysis

The infrared spectra of the raw biomass (a), pre-treated algae before (b), and after (c) Fe^{3+} biosorption were obtained using Fourier Transform Infrared (Bruker Vertex 70 FT-IR spectrophotometer). Fig. 6 shows the FTIR-ATR spectra of *Sargassum Vulgare* before and after surface modification. Results for Fe^{3+} loaded modified algae are also shown. It was observed that minor changes can be seen in the spectrum of untreated and treated algae, which indicates the presence of similar functional groups. The broadband displayed in the region of 3000–3500 cm^{-1} indicates the presence of –OH and –NH groups. The peak observed at 2920 cm^{-1} was assigned to the C–H stretching vibrations of the aliphatic groups [42]. The absorbance peaks appear at 1722 cm^{-1} attributed to the stretching band of the free carbonyl double bond. The absorbance bands at 1620 cm^{-1} are related to the stretching of the carboxylate ions [43]. The weaker band at 1411 cm^{-1} represents the presence of C-H band, and the band at 1361 cm^{-1} is attributed to the asymmetric $-SO_3$ stretching which was not present in raw (untreated) biomass [44]. The peaks at 1217 and 1163 cm^{-1} correspond to the carbonyl C–O bond and to the symmetric stretching of SO_3, respectively. The peak at 1026 cm^{-1} could be assigned to the stretching vibration of C–O of alcoholic groups. Finally, a peak at 811 cm^{-1} may correspond to S=O stretching [39]. Compared with the spectra algae before biosorption, the peak at 1606 cm^{-1} was found to be shifted to 1620 cm^{-1}, but most peaks are unchanged.

Scanning electron microscopy

The SEM analysis of raw algae, NaCl pre-treated *Sargassum Vulgare,* and after biosorption of Fe^{3+} is given in Fig. 8 (A, B, and C). As expected, the alga surface morphology presents significant differences after modification. The surface microstructures after modification turned deeper and smothered, which may be due to the NaCl treatment. Furthermore, algae surface morphology presents significant modification after Fe^{3+} and the biosorption process might be created on the granular structure of the algae surface.

Thermodynamic studies

The thermodynamic parameters obtained for Fe^{3+} biosorption onto pre-treated biomass are listed in Table 3.
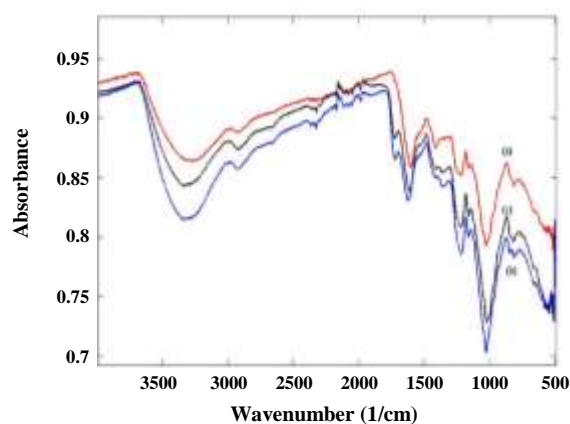

Fig. 6: FT-IR spectra of raw Sargassum Vulgare (a), NaCl modified before (b) and afterFe^{3+} biosorption (c).

The negative values of ΔG^0 indicate that the biosorption of Fe^{3+} on algae biomass is spontaneous. The negative value of ΔH^0 suggests that the process is exothermic. The negative entropy value (ΔS^0), −0.062 kJ mol^{-1} K^{-1}, suggests a decrease in the randomness at the S/L interface during the sorption of Fe^{3+} onto *Sargassum Vulgare* [45].

Desorption study

For the desorption of Fe^{3+} ion from NaCl-modified algae, three desorbing solutions (0.1M HNO_3, 0.1M HCl, and 0.001M EDTA) were used. The cycles of sorption-desorption were repeated thrice, the biomass biosorption capacity was evaluated at a pH = 2. The results of the desorption experiments are listed in Table 4. The best desorption capacity was observed for 0.001 M EDTA (close to 90 %). Nevertheless, it is clear that as the number of sorption-desorption cycles increases the regeneration of the biomass becomes less efficient.

CONCLUSIONS

The present study reveals that brown algae (*Sargassum Vulgare*) biomass, modified by a pre-treatment using NaCl, for the removal of Fe^{3+}, follows the Langmuir isotherm model. The sorption capacity, as measured by the maximum sorption capacity of the Langmuir model, is increased by more than 50 % as compared to that of the raw (without pre-treatment) algae. The biosorption process follows a pseudo-first-order kinetic model. The thermodynamic parameters confirmed a feasible, spontaneous

Table 3: Thermodynamic parameters.

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (KJ/mol.K)
298	-11.48	-22.10	-0.062
308	-7.08		
318	-7.00		

Table 4: Influence of different desorbent solutions on Fe^{3+} on NaCl modified algae.

Cycle	Fe^{3+} recovery (%)		
	0.001 M EDTA	0.1 M HCl	0.1 M HNO$_3$
1	88.86	68.86	69.25
2	61.14	62.07	24.77
3	27.51	12.56	5.56
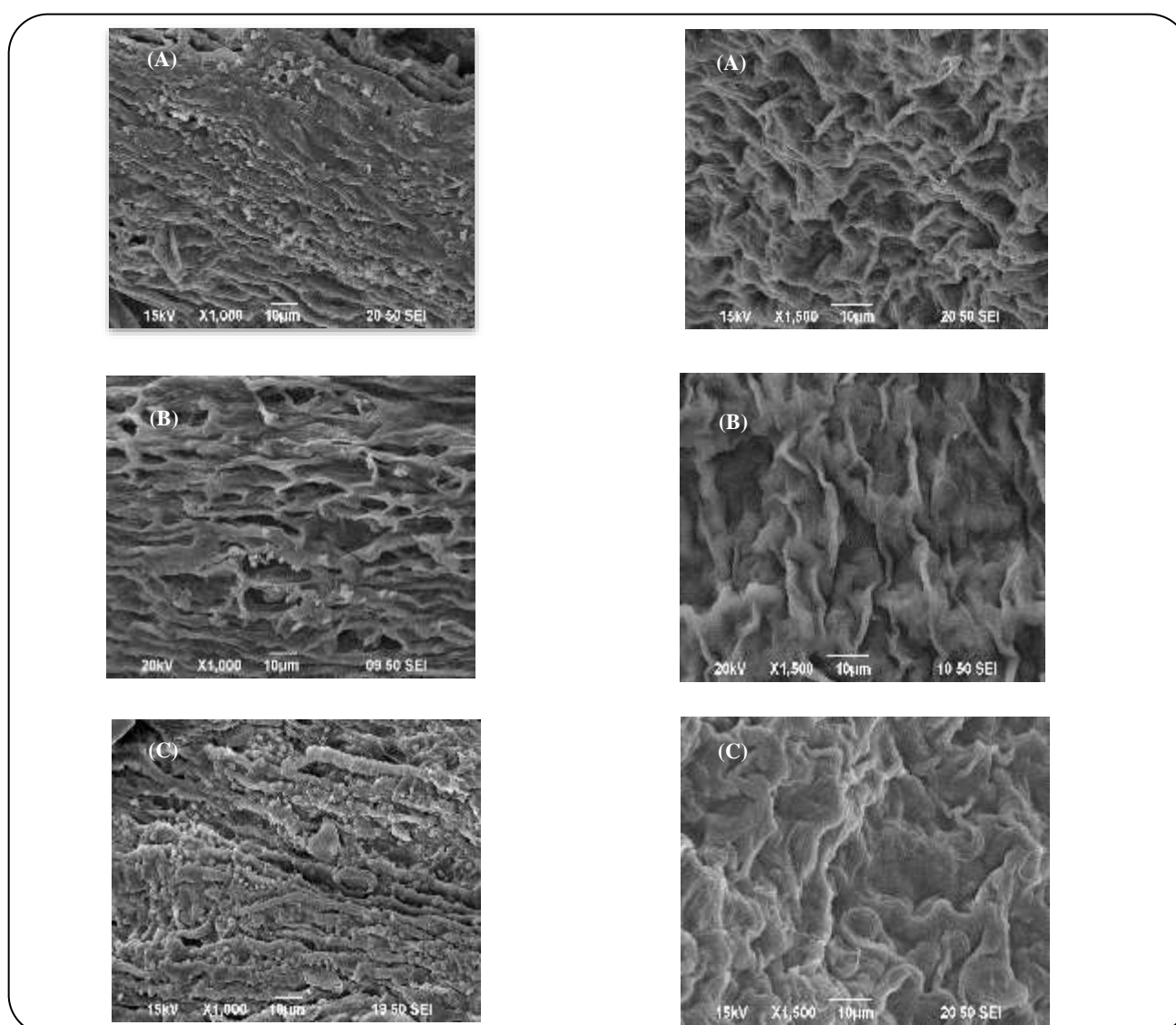
Fig. 7: SEM micrographs of Raw algae (A). NaCl-modified algae before biosorption of Fe^{3+} (B) NaCl-modified algae after biosorption of Fe^{3+} (C).

exothermic process. The sorption-desorption studies revealed that EDTA is the best desorbing agent among those essayed for the reuse of biomass, although the regeneration efficiency decreases with the number of cycles. In summary, the use of NaCl-modified algae presents several advantages as a low-cost biosorbent material for the treatment of wastewater contaminated with Fe^{3+}.

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