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Biosorption of Fe (III) from aqueous solution using brown algae *Sargassum Vulgare*

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Abstract

The presence of metal ions in aqueous solutions represents, nowadays a major environmental problem. The presence study investigates the potential adsorption capacity of Sargassum vulgare for the removal of iron (III) ions from aqueous solution. The elaborated adsorbent was characterized using FTIR analysis, in order to reveal the presence of functional groups. Batch adsorption experiments were carried out to evaluate the effect of process parameter such as pH, contact time and adsorbent dosage on removal capacity. The optimum removal of iron (III) ions was obtained at pH 3, adsorbent dose of 5 g/L and equilibrium time of 120 min. Kinetic data were successfully described with pseudo-first order and pseudo-second order models. The results showed that the kinetic biosorption process of Fe (III) followed pseudo first order with ($R^2 = 0.99$ and $k = 0.056$). The biosorption equilibrium was studied using Langmuir and Freundlich models. Biosorption of Iron (III) onto *Sargassum vulgare* biomass followed the Langmuir isotherm ($R^2 = 0.99$) with a maximum biosorption capacity of (q_e= 63.67 mg/g).

Keywords: Biosorption, Iron, algae, Kinetic, Isotherm

Introduction

In recent years, industrial activities have increased production of heterogeneous wastewater, loaded with heavy metals such as Cd, Cu, Cr, Zn, Fe, often considered among the major source of pollution [1]. Heavy metals do not degrade into harmless end products and are generally accumulated along the food chain (water–plants–animals–humans), thus, posing a great threat to living organisms. The treatment of these effluents shows a great scientific interest. Indeed several techniques such as reverse osmosis, chemical precipitation, ion exchange, membrane separation [2. 3] have been used to remove heavy metals. However, they are primarily useful for high concentrations of metals, owing cost and the generation of sludge.[4].In this sense biosorption turn out an efficient method for the removal of heavy metals from industrial wastewater, due to its high efficiency, low cost, minimization of chemical and biological sludge biosrobent regenerability, and the possibility of metal recover [5].Serval biosorbents were studied in the literature such as bacteria, Fungie, algae, fruit waste, etc. Algae have proven to be the most efficient and economical biosorbent, for metals removal. Specifically brown algae have shown a high removal capacity, due to its macroscopic structures and cell wall properties (alginate, fucoidan) which are primarily responsible for the binding of these metals. [6.7.8.10]

The aim of the present work is to investigate the iron biosorption by dead sargassum vulgare by evaluating the influence of various parameters such as pH, contact time, and the amount of biomass on the removal capacity. The functional groups involved in metal biosorption were identified using FTIR analysis. The biosorption kinetic was modeled by using the first and second order models. Experimental data of biosorption are modeled by the Langmuir and Freundlich model.

2. Materials and methods

2.1. Preparation of biosorbent

The brown algae (Sargassum Vulgare) biomass was used as biosorbent for the application previously described. The alga was collected from the coast of Martil, North of Morocco. The biomass was washed three times firstly with tap water and then with deionized water, in order to remove the impurities and salts. Subsequently, it was sundried for 48h and heated in an oven at 60°C for 24h. The dried alga biomass was crushed and sieved to a particle size ranging from (0.2-1 mm). Biomass was stored in transparent bottles until use.

2.2. Preparation of Fe (III) stock solutions

The stock solution of iron (III) (1g / L) was prepared by dissolving the adequate quantity of ammonium iron (III) sulphate dodecahydrat in deionized water. The concentration range of iron prepared by the diluting of stock solution varies between 3 and 800 mg/L. 0.1M HCl and 0.1M NaOH solution was used to adjust the pH of the dissolution.

2.3. IR spectra

FTIR spectroscopy was used to identify the chemical functional groups present in the raw biomass and Fe-loaded biomass using 640-IR FT-IR Spectrometer.

2.4. Batch experiment studies

The biosorption of iron (III) on the obtained biomass was performed in a batch system. In the present work several effects on the biosorption of iron were studied, such as the initial pH, the contact time and kinetic and equilibrium parameters. The effect of pH was studied by performing series of experiments at a pH ranging from 1.5 to 4.A solution of 0.1 M HCl and 0.1 M NaOH was used to adjust the pH of the dissolution at room temperature. The kinetic study of the biosorption of Fe (III) was carried out in glass bottles containing 100 ml of Fe (III) with a concentration of 100 mg /L mixed with 0.5 g of dried biomass. The pH was adjusted to the optimum value and the bottles remain in agitation using KS 4000 ic control (150 rpm) for 4h at 25 °C. Aliquots of 2 ml were taken every 5 min for the first 30 minutes then every 10 min, and then every 30 min for the rest of the experience. Next the samples were filtered and analyzed by measuring the absorbance using Varian Cary 50 Bio UV/ Visible Spectrophotometer in order to determine the variation of the iron concentration as a function of time using thiocyanate method the value of λ_{max} was reached at 465 nm.

The equilibrium study of Fe (III) removal was performed in glass bottles containing different concentrations of iron (3 - 800 mg/L) and 5 g/L of dried biomass.

The bottles are placed in agitation (150 rpm) for 2 h (Equilibrium time of biosorption) at room temperature. The initial pH is adjusted as described above and finally an appropriate volume recovered, filtered and analyzed by measuring the absorbance.

2.4. Metal uptake

The amount of adsorbed Fe (III) per unit of biosorbent (mg metal ions/g dry adsorbent) was determined by using the following expression:

$$q = \frac{(C_i - C_f)}{M} \cdot V \qquad (1)$$

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

$$\% \mathrm{Re}moval = \frac{(C_i - C_f)}{C_i} \cdot 100 \qquad (2)$$

3. Results and discussion

3.1. FTIR spectral analysis.

Biosorption in algae may mainly be attributed to the cell wall structure containing functional groups such as amino, hydroxyl, carboxyl and sulfate. The main substances of this type in brown alga are generally alginates, which usually constitute around 10 – 40% [8] of the total dry weight, and some sulfated polysaccharides [9.10]

The FT-IR analysis was performed to obtain information about the interaction between the functional groups of biomass and Fe (III) ions. The FT-IR spectra algal biomass, before and after iron treatment are shown in Figure.1.The broad vibration around 3000 – 3600 cm^{-1} is indicative of the presence of the -OH and -NH groups on algal biomass. The peak around 2900 cm^{-1} could be assigned to the C-H stretch. The wide peak at 1641.5 cm^{-1}

can be attributed to the stretching vibration of carboxyl group (-C = O). The peak at 1426.9 cm^{-1} represents –N-H bending vibration for Sargassum vulgare. The band about 1247 cm^{-1}, represents SO_3 stretching. The bands observed at 1057.6–1161.3 cm^{-1} were assigned to C-O stretching vibration of alcohols and carboxylic acids. [11.12]

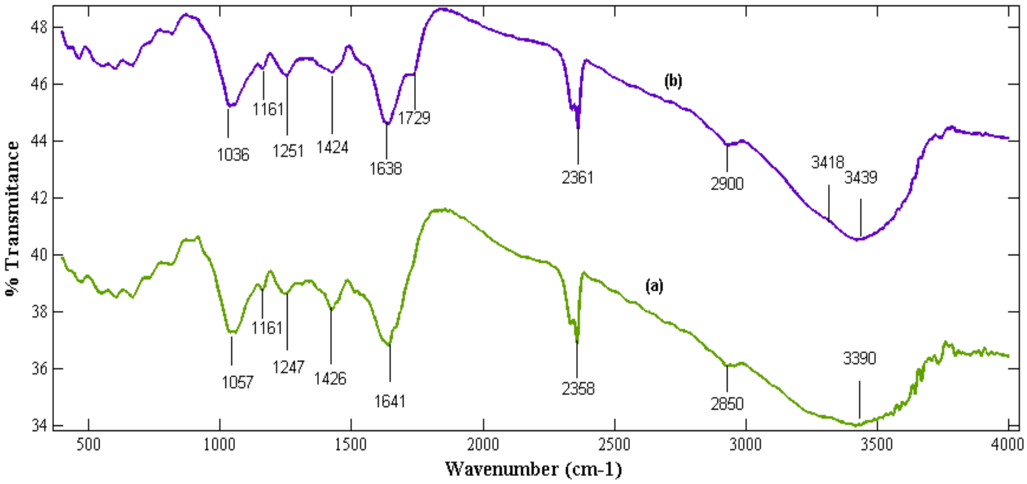

Figure1. FT-IR spectra of algae (a) before biosorption, (b) after biosorption

By comparing iron loaded biomass with FTIR spectra of pure biomass significant the changes in some peaks can be displayed. As can be seen in Figure.1b, the change at 3418.6 cm $^{-1}$ suggests the major role of -OH and -NH group for Fe (III) biosorption onto Sargassum biomass. The significant reduction in the peak at 1638 cm^{-1} reflects the effect of binding of Fe (III) ions upon carboxyl groups. These observations indicate that several functional groups (hydroxyl, carboxyl, and amine) on the surface of the biosorbent are responsible for the iron binding.

3.2. *Effect of pH*

Several factors may influence the process of biosorption. Indeed, the pH is a very important variable on this process, once it affects the metal chemical speciation, the activity of biomass functional groups (active sites), and the ion metallic competition for active sites [9]. In this sense, the effect of initial pH on the removal of Fe (III) onto sargassum vulgare was studied .In this experiment, the pH was varied from 1.5 to 4 at a temperature of 25C°. A concentration of Fe (III) of 100 mg / L and an amount of biomass of 5g / L were used. The obtained results are shown in Figure 2.

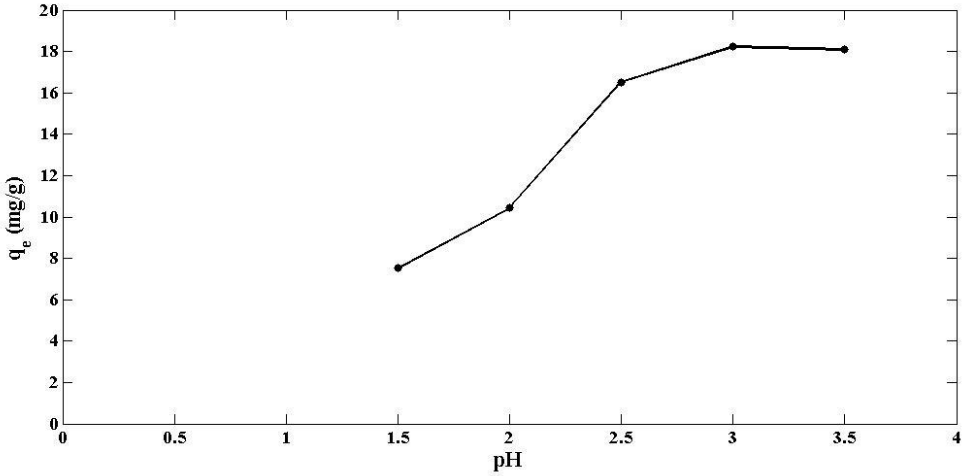

Figure2. Effect of pH on adsorption of Fe (III) onto Sargassum Vulgare (T = 25 °C, algal dosage = 5 g / l, Iron concentration = 100 mg /l).

It can be seen an increases of iron removal with the increasing pH up to a value of 3,5. However, at pH 4 the beginning of the precipitation of iron solution and the formation of iron hydroxide Fe (III) were observed. The maximum biosorption of Fe (III) ions on Sargassum vulgare was reached at pH 3 [13,14]. According to the literature [15-17].Therefore, pH of 3 was chosen to optimize the adsorption conditions, and to avoid the precipitation of iron, for further experiments.

3.3. Effect of contact time

Contact time is an important factor influencing the biosorption equilibrium of iron (III). During the experiment, different biosorption parameters such as concentration of iron (100 mg /l), biosorbent dose (0.5 g) , pH of (3), Temperature (25°C) were kept constant, and the contact time was varied from 3 to 240 min. As shown in Figure 2, the removal percentage of iron increased with the increasing of contact time. The kinetic of iron biosorption was very fast initially for a period of 15 and 30 min with 56% and 79% respectively, this behavior can be due to the availability of active sites on the surface of the biomass, and that the solution concentration is higher at the beginning of the experiment. [1.18.19].The biosorption equilibrium was reached at 60 min with 96% of iron removal. Then, the elimination becomes very slow may be due to the saturation of binding sites. [20-22].Indeed, several works show that most algae reach the maximum elimination of metal ions between 30 and 90 min [10.23.24]. For the rest of the experiments, 120 min is chosen as an optimum time for biosorption of iron.

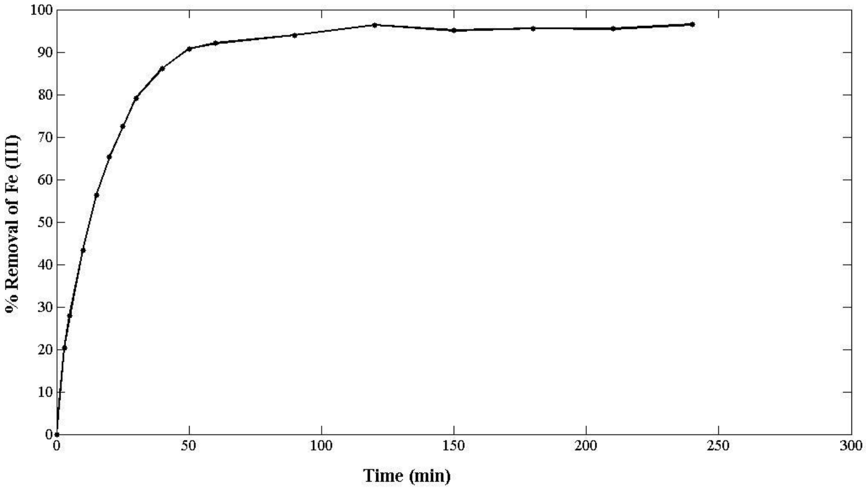

Figure3. Effect of contact time on Fe (III) biosorption on Sargassum vulgare.(pH =3, T =25 °C, Algal dose= 5 g / l, Ci= 100 mg /l).

3.4. Effect of algae dose

The removal of metal ions by inactive biomass is based on metal sorption due to the high affinity between the metal ions and the biomass [10].To investigate the effect of the biosorbent dose on the elimination of iron, an amount from 0.1g to 1g (1g/L - 10g/L) was mixed with 100 ml of the iron solution with a concentration of 100mg / L. The biosorption percentage and capacity of iron versus the amount of algae biomass are plotted in (Figure 4). According the results plotted in this figure-4, an increase of the biomass quantity from 1g/L to 5g/L causes an improvement of iron removal efficiency from 40 % to 96% respectively, which can be related with the high external surface and the availability of active adsorption sites [25.26]. Indeed, when a high quantity of biomass is used there is no observed change due the metal disappearance from the solution. So, the chosen amount of biomass is able to eliminate these iron concentration [27.28].

3.5. Kinetic study

Adsorption kinetic depends on the sorbate–sorbent interactions and operating conditions. Several kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism. In this study, experimental data were analyzed using the non linear form for two kinetic models: pseudo-first-order and pseudo-second-order models [29].

The pseudo-first-order rate equation of Lagergren (1898) used for the adsorption of solute from a liquid solution was applied to Fe (III) ions biosorption using the following expression [30.31]:

$$\frac{dq(t)}{dt} = k_1\left(q_{eq} - q(t)\right) \qquad (3)$$

After integration of this for the boundary conditions t = 0 to t = qt = 0 t∞ and Qt = qe, Eq. (3) must be expressed as the following:

$$q(t) = q_{eq}(1 - \exp^{-k1*t}) \qquad (4)$$

Where k1 is the rate constant of pseudo-first order sorption (g/mg/min), q_{eq} is the amount of solute sorbed at equilibrium (mg/g), q_{eq} is the amount of solute sorbed on the surface of the sorbent at any time t (mg/g).

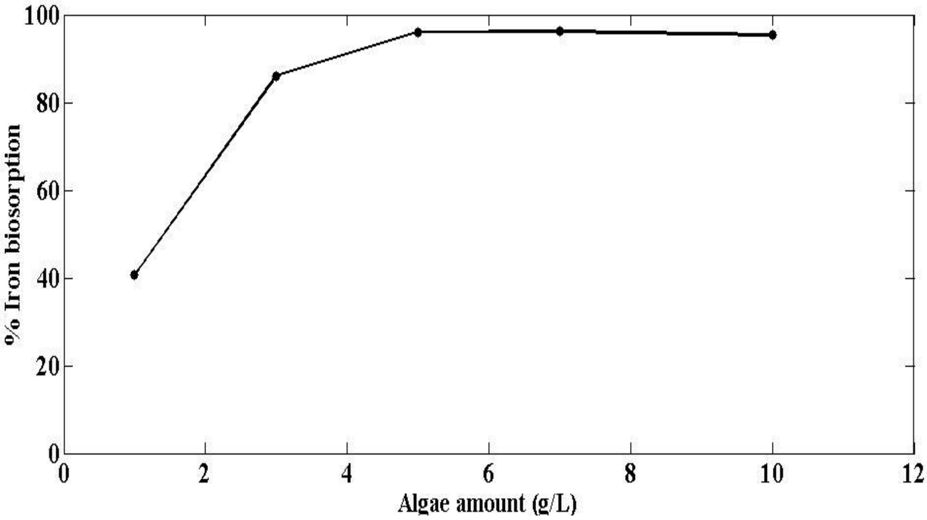

Figure 4. Effect of algae amount on the removal of iron (III) (initial iron concentration = 100mg/L, pH =3, temperature = 25±2 ◦C).

The Ho and McKay pseudo-second-order equation which is given in the following form [32 33].

$$\frac{dq(t)}{d(t)} = k_2(q_{eq} - q(t)) \qquad (5)$$

After integration the equation 5 becomes

$$q(t) = \frac{q^2{}_{eq}k_2t}{1 + q_{eq}k_2t} \qquad (6)$$

Where q_{eq} (mg/g) is the sorption capacity at equilibrium (calculated value from experimental data), k_2 (g/mg/min) is the pseudo-second order rate constant.

Both models were applied to experimental data and the obtained are shown in Figure 5 and Table 1.Various parameters were obtained after fitting curve as R^2, k_1, k_2 and qe [16.24]. The obtained correlation coefficient (R^2) can help to decide the suitable model. According to the results of Table 1, the R^2 corresponding to the pseudo first order is higher than R^2 of the pseudo second order, which means that kinetic of iron biosorption follows the first order models.

3.6. Biosorption Isotherm

Several models of adsorption isotherms have been used to describe the relationship between adsorption equilibrium, the adsorbed amount and solute concentration at a given temperature. In this context two different isotherm models: (Langmuir and Freundlich) were used in order to determine the biosorption equilibrium of iron with different concentrations ranging from 3mg/L to 800 mg/L, and a fixed amount of alga biomass (5g/L).The Langmuir model generally used to quantify and compare the performance of different biosorbent. This model assumes that adsorption occurs on a homogeneous monolayer surface without lateral interaction between molecules adsorbed even on adjacent sites, and the energy of adsorption is uniform without transmigration of the adsorbent.[34,35,26]

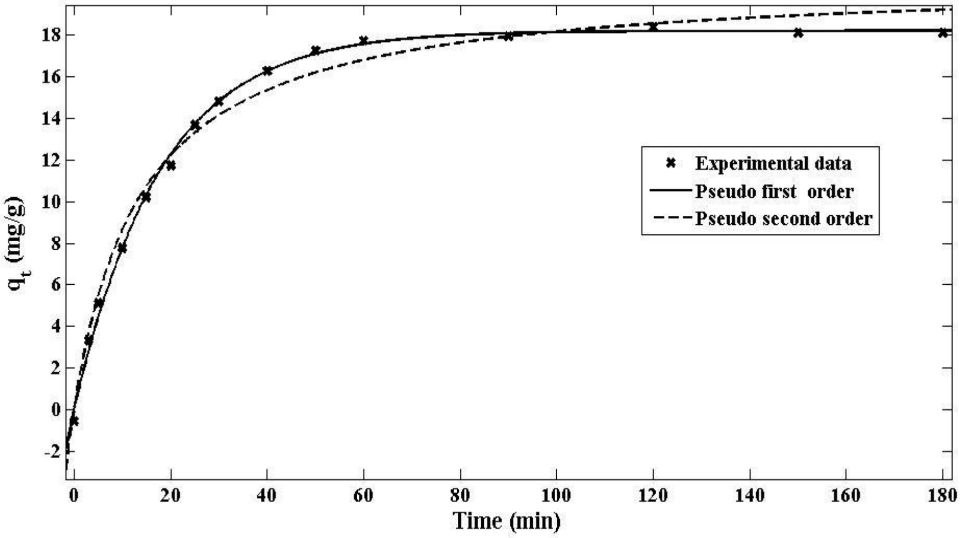

Figure 5. Kinetics of Iron (III) biosorption by raw Sargassum Vulgare biomasses (Metal concentration=100 mg/L; pH=3, T= 25±2 ◦C, Time=120min).

Table1. Kinetic constants for the biosorption of Fe (III) in batch systems from pseudo-first order, Pseudo second order

Kinetic parameters	**Pseudo first order**	**Pseudo second order**
k (g/mg/min)	0.05605	0.003853
q_e (mg/g)	18.17	20.12
R^2	0.9975	0.9843

Nonlinear form of Langmuir model is given as

$$qe = qm\frac{(bC_e)}{(1+bC_e)} \qquad (7)$$

Where *q*e is the adsorbed metal ion quantity per gram of biomass at equilibrium (mg g−1); *q*m the maximum amount of metal ion per unit weight of biomass to form a complete monolayer on the surface bound at high *C*e (mg g−1); *b* a constant related to the affinity of the binding sites (l mg−1).
Freundlich model can be applied to a multilayer adsorption on a heterogeneous surface, along with interaction between the adsorbed molecules. [27.34]
Nonlinear form of Freundlich model is given as

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

Where k_f and n are the Freundlich's constants characteristic of the system.

Table2. Isotherm parameters for the biosorption of iron (III)

Biosorbent	**Langmuir parameters**			**Freundlich parameters**		
Dried Sargassum Vulgare	qm (mg/g)	b	R^2	k_f	n	R^2
	63,67	0,068	0,956	9,148	3,001	0,865

The results of the modeling curve for both isotherms are shown in Figures 6 and 7.Constants and correlation coefficients are presented in Table 2. It can be seen that the adjustment of the Langmuir equation leads to the best experimental data with a coefficient of 0.95. However, with Freundlich model a coefficient of 0.86 is obtained. Therefore, it can be deduced that the studied process of the biosorption follows the Langmuir model, according other studies [2.36.37.].

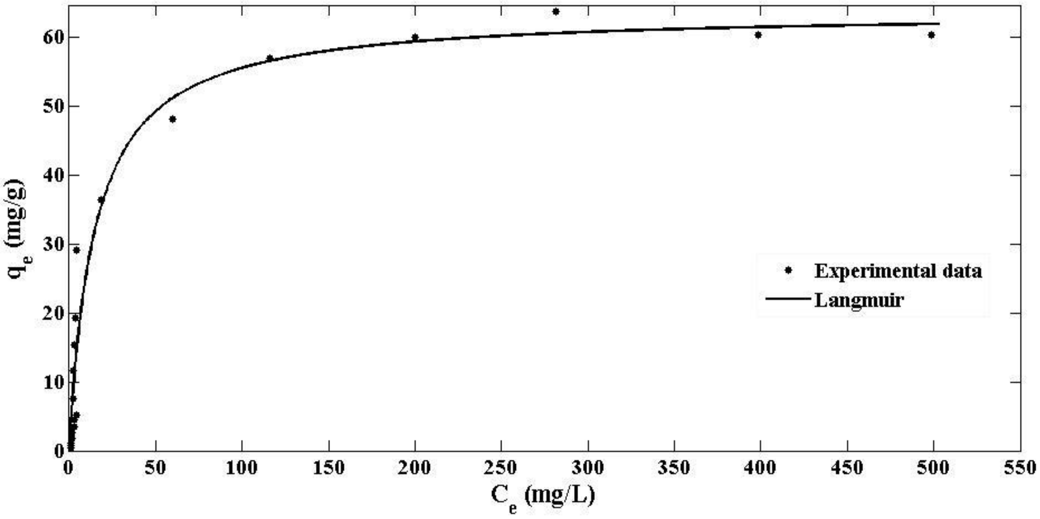

Figure 6. Langmuir isotherm model

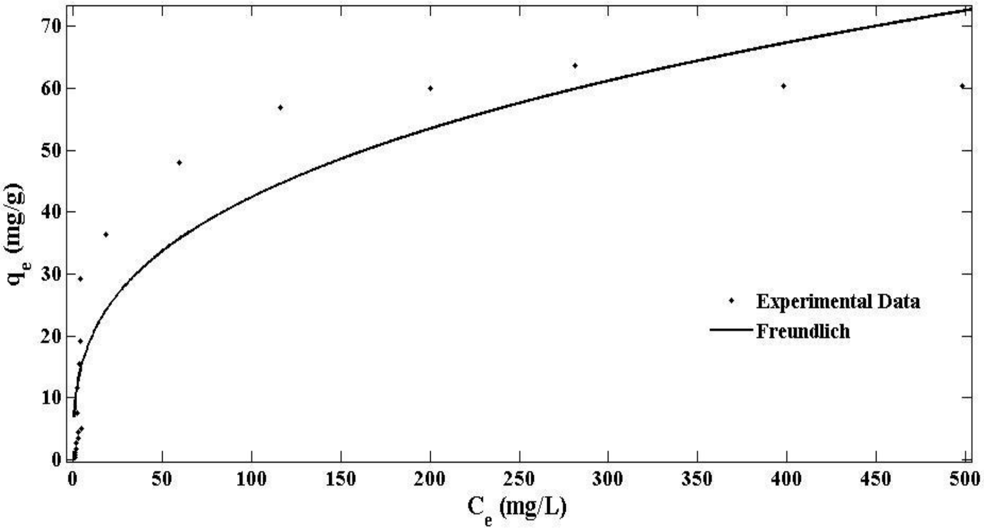

Figure7. Freundlich isotherm model

Conclusion

This paper presents a study focused on biosorption of Fe (III) from aqueous solution using the Sargassum vulgare as a low cost biosorbent. The cell walls of this brown alga contain anionic groups such as (–COO, –C–O, –NH, –C=O, –OH), whose adsorbant ability towards Fe3+ ions is rather high. Adsorption is moreover influenced by various parameters such as initial pH, initial Fe3+ concentration, and biomass quantity. The experimental data were analyzed using Langmuir and Freundlich models. The kinetic data were analyzed using pseudo-first order and pseudo-second order. Furthermore, it can be concluded that Sargassum vulgare can be considered as an alternative adsorbent for the treatment of wastewater containing Fe (III) ions, due to its low-cost and high sorption capacity.

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