

Removal of copper from aqueous solution using *Ulva fasciata* sp.—A marine green algae

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Abstract

Batch adsorption experiments were carried out for the removal of copper from its aqueous solution using *Ulva fasciata* sp. a marine green algae as adsorbent. The adsorption of Cu(II) by *Ulva fasciata* sp. was investigated as a function of pH, contact time, initial Cu(II) and adsorbent concentrations and adsorbent size. About 0.1 g of *Ulva fasciata* sp. was found to be enough to remove 95% of 20 mg/L copper from 30 mL aqueous solution in 20 min. The optimum pH value was found to be 5. The dynamic data fitted to the pseudo-second order kinetic model. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were determined. The experimental adsorption data were fitted to the Langmuir adsorption model. The maximum adsorption capacity was 26.88 mg/g. The applicability of Lagergren kinetic model was also investigated.

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1. Introduction

The release of heavy metals into the environment by industrial activities is a serious environmental problem because they tend to remain indefinitely, circulating and eventually accumulating throughout the food chain [1,2]. Different conventional processes (precipitation, ion exchange, electrochemical processes and/or membrane processes) are usually applied to the treatment of industrial effluents but the application of such processes is often limited because of technical or economic constraints [3].

Adsorption of heavy metals is one of the possible alternative technologies involved in the removal of toxic metals from industrial waste streams and natural waters using low-cost adsorbents. It is a potential and interesting alternative to conventional processes for the removal of metals, such as ion exchange processes [4,5]. It is a rapid, reversible, economical and ecofriendly technology in contrast to conventional chemical methods of

removing metal ions from industrial effluents. Adsorption of metal ions from aquatic system using microbial biomass, including algae, fungi and bacteria has gained importance in recent years [6,7].

Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate [8]. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well. The excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems, kidney damage, anemia and continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers [8,9]. For these reasons EPA (U.S.A.) has regulated drinking water concentrations not to exceed 1.3 ppm for copper [10].

Although thousands of species of algae have been identified during the last 200 years, very few have been investigated to determine their absolute or relative abilities to sequester toxic heavy metal ions. In the few, limited studies where species have been compared, results often reveal major differences in metal binding efficacy between species and even among strains of a single species, for any given metal and/or set of physicochemical conditions [11].

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Equilibrium data presented as adsorption isotherms, Langmuir, Freundlich etc., are the main requirements for the design of adsorption systems. Obtaining equilibrium data for a specific sorbate/sorbent system can be carried out experimentally, with a time-consuming procedure that is incompatible with the growing need for adsorption systems design [12].

The aim of the present study is to remove copper from its aqueous solution using *Ulva fasciata* sp. a marine green algae as adsorbent material for various parameters like pH, contact time, initial Cu(II) concentration, adsorbent concentration and adsorbent size. This algae was chosen as adsorbent because of availability of very meager information about their adsorption abilities. The adsorption capacity of this at room temperature was estimated using equilibrium studies.

2. Materials and methods

2.1. Preparation of adsorbent

The green colored marine algae *Ulva fasciata* sp. used in the present study were collected from the coastal belt of Visakhapatnam, Andhra Pradesh, India. The collected algae were washed with deionized water several times to remove impurities. The washing process was continued till the wash water contains no dirt. The washed algae were then completely dried in sunlight for 10 days. The resulting product was directly used as adsorbent. The dried algae were then cut into small pieces and were powdered using domestic mixer. In the present study the powdered materials in the range of 75–212 μm particle size were then directly used as adsorbents without any pretreatment.

2.2. Chemical and metal solution

Stock solution of copper concentration 1000 mg/L was prepared by dissolving 3.93 g of 100% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck) in 1000 mL of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 20 and 100 mg/L and they were prepared by diluting the copper stock solution, which were obtained by dissolving in deionized water.

2.3. Analysis

The total metal concentration in solution was determined with atomic absorption spectrophotometer (GBC Avanta Ver 1.32, Australia) at a wave length of 327.4 nm, slit width 0.2 nm and lamp current 3 mA.

2.4. Experimental

For obtaining the adsorption equilibrium data for the adsorption of copper on *Ulva fasciata* sp. the experiment was carried as a function of the contact time, initial pH, initial metal ion concentration and adsorbent dosage. The adsorption experiments were carried out in a batch process under the following experimental conditions.

Initial copper concentration (mg/L)	20, 40, 60, 80 and 100
Adsorbent concentration (g/L)	0.1, 0.2, 0.3, 0.4 and 0.5
pH	2, 3, 4, 5, 6, 7, 8, 9 and 10
Particle size (μm)	75–212

Batch adsorption equilibrium experiments were conducted in 250 mL conical flasks at a constant shaking speed (180 rpm). All the experiments were carried out at room temperature ($28 \pm 2^\circ\text{C}$). The concentration of copper metal ions in solution before and after adsorption was determined using Atomic Absorption Spectrophotometer by monitoring the absorbance for the metal ion used.

The amount of adsorption at equilibrium q_{eq} (mg/g) and the percent adsorption (%) were computed as follows:

$$q_{\text{eq}} = \frac{[(C_0 - C_{\text{eq}})V]}{X}$$

$$\text{Percent adsorption (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C_{eq} are the initial and equilibrium concentrations (mg/L), V volume of solution, X the weight of *Ulva fasciata* sp. (g) and C the solution concentration at the end of adsorption.

2.5. Adsorption equilibrium

Equilibrium studies were carried out by agitating 30 mL of copper solutions of initial concentrations varying from 20 to 100 mg/L with 0.1–0.5 g of algae at room temperature for 20 min at a constant stirring speed at a pH of 5.

During the adsorption, a rapid equilibrium is established between adsorbed metal ions on the algal cell (q_e) and unadsorbed metal ions in solution (C_{eq}). This equilibrium can be represented by the Langmuir [13] or Freundlich [14] adsorption isotherms, which are widely used to analyse data for water and wastewater treatment applications. The Langmuir equation which is valid for monolayer adsorption on to a surface a finite number of identical sites and is given by

$$q_e = \frac{Q_{\text{max}} b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (1)$$

where Q_{max} is the maximum amount of the metal ion per unit weight of algae to form a complete monolayer on the surface bound at high C_{eq} (mg/g), and b is a constant related to the affinity of the binding sites (L/mg) Q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. Q_{max} and b can be determined from the linear plot of C_{eq}/q_e versus C_{eq} [13–15].

The empirical Freundlich equation based on adsorption on a heterogeneous surface is given by

$$q_e = K_F C_{\text{eq}}^n \quad (2)$$

where K_F and n are Freundlich constants characteristic of the system. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. Eq. (2) can be linearized in

logarithmic form and Freundlich constants can be determined. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model [15–19].

3. Results and discussion

3.1. The effect of pH

pH is one of the most important environmental factor influencing not only site dissociation, but also the solution chemistry of the heavy metals; hydrolysis, complexation by organic and/or inorganic ligands. Redox reactions, precipitation are strongly influenced by pH and, on the other side, strongly influence the speciation and the biosorption availability of the heavy metals [20]. The pH value of the solution was an important controlling parameter in the adsorption process. Fig. 1 shows the effect of pH value of solution on the adsorption of copper on the *Ulva fasciata* sp. at room temperature, 20–100 mg/L of initial metal ion concentration and 0.1 g of adsorbent dosage. The percentage adsorption increased from 7.52 to 96.43% for an initial concentration of 20 mg/L with an increase in solution pH from 2 to 5. It shows that the adsorption capacity of copper onto *Ulva fasciata* sp. increases significantly with increasing pH. The maximum removal of copper for contact time 20 min was carried out at pH 5. But for pH values from 6 to 10 lower adsorption capacity was observed for copper, this might be due to the precipitation and lower polarity of copper(II) ions at higher pH values. At low pH values, the surface of adsorbent would also be surrounded by hydronium ions, which decrease the copper interaction with binding sites of the *Ulva fasciata* sp. by greater repulsive forces. As the pH increased, the overall surface on the *Ulva fasciata* sp. became negative and adsorption increased. In this study, these copper cations at around pH 5 would be expected to interact more strongly with the negatively charged binding sites in *Ulva fasciata* sp. As a result, the optimum pH for copper adsorption was found as 5 and the other adsorption experiments were performed at this pH value.

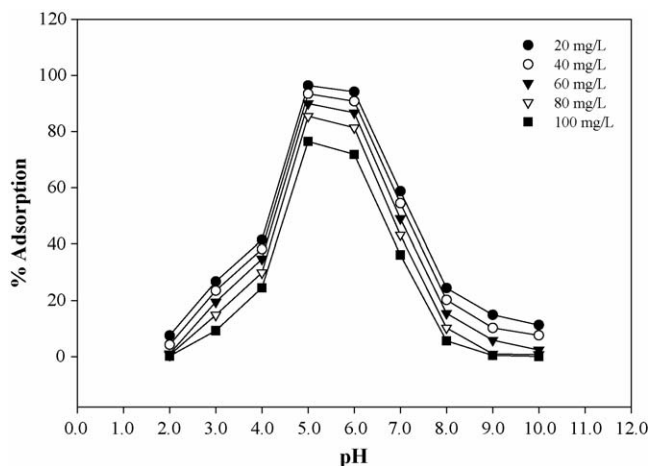


Fig. 1. Effect of pH on the % adsorption (initial metal concentration = 20–100 mg/L, adsorbent concentration = 0.1 g/30 mL, adsorbent size = 75 μ m).

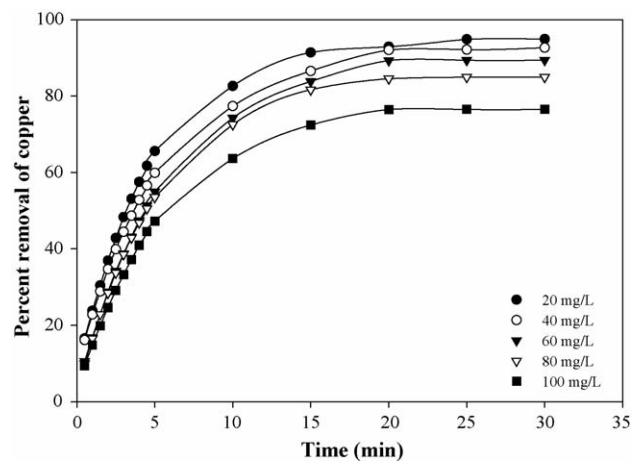


Fig. 2. Effect of contact time on the percentage removal of copper (pH 5, adsorbent concentration = 0.1 g/30 mL, adsorbent size = 75 μ m).

The effect of pH on the adsorption of copper has been investigated by various investigators using a variety of different adsorbent/sorbent types [21–23]. Optimum adsorption capacity of copper at pH 5 has been reported on sphagnum moss peat [21], *Padina* sp. [22], active carbon obtained from almond shell, olive and peach stones [23].

3.2. The effect of contact time

The data obtained from the adsorption of copper ions on the *Ulva fasciata* sp. showed that a contact time of 20 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and unadsorbed copper concentrations at the end of 20 min are given as the equilibrium values (q_e , mg/g; C_{eq} , g/L), respectively (Fig. 2).

3.3. Effect of algae concentration

Fig. 3 shows the effect of algae concentration on the amount of copper adsorbed, q_e (mg/g) and on the % removed at equi-

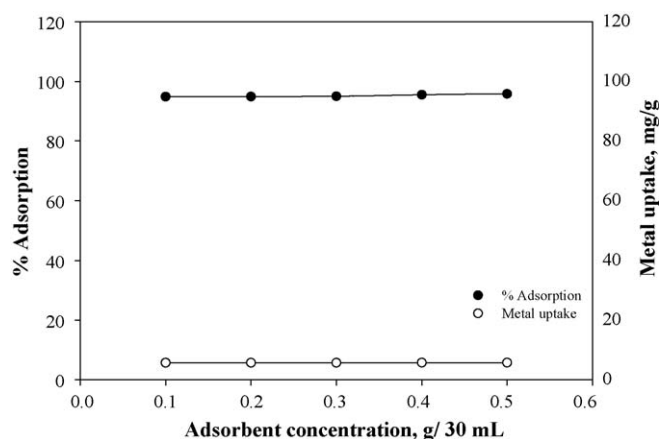


Fig. 3. Effect of adsorbent concentration on percentage adsorption and metal uptake (pH 5, initial metal concentration = 20 mg/L, adsorbent size = 75 μ m).

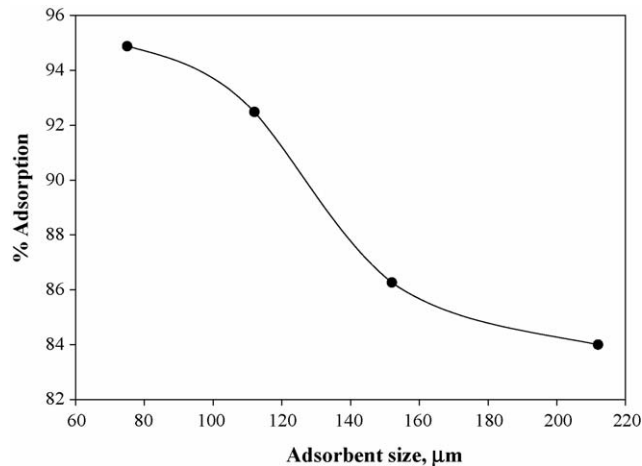


Fig. 4. Effect of adsorbent size on percentage adsorption (pH 5, initial metal concentration = 20 mg/L, adsorbent concentration = 0.1 g/30 mL).

librium conditions. It was observed that the amount of copper adsorbed varied with varying algae concentration. The amount of copper adsorbed increases with an increase in adsorbent dosage from 0.1 to 0.5 g. The percentage copper removal was increased from 94.88 to 95.86% for an increase in biomass concentration from 0.1 to 0.5 g. The increase in the adsorption of the amount of solute is obvious due to increasing biomass surface area.

3.4. Effect of particle size

The effect of different adsorbent particle sizes on percentage removal of copper is investigated and showed in Fig. 4. It reveals that the adsorption of copper on *Ulva fasciata* sp. decrease from 94.88 to 84% with the increased particle size from 75 to 212 μm . The smallest size obtained was 75 μm due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity.

3.5. Adsorption kinetics

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig. 5 shows the plot between amount adsorbed, q_t (mg/g) versus time, t (min) for different initial solute concentrations. From the figure it was observed that q_t value increased with increase in initial copper concentration. But however the adsorption rates within the first 5 min was observed to be very high and thereafter the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after equilibrium. The saturation time was found to be 20 min based on the initial metal concentration. The kinetics of the adsorption data was analysed using two kinetic models, pseudo-first order and pseudo-second order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows.

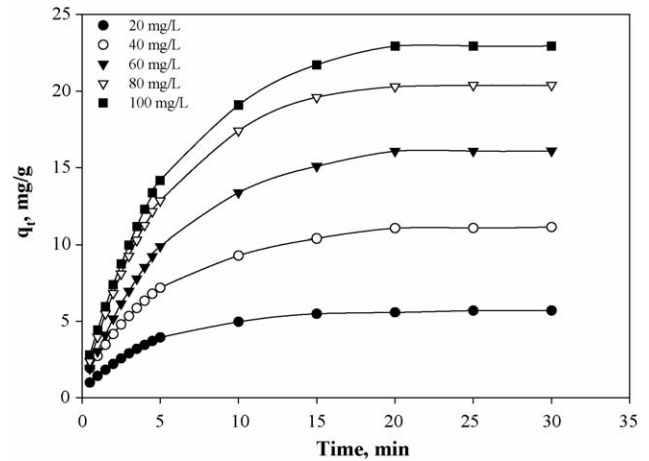


Fig. 5. Adsorption kinetics for copper onto *Ulva fasciata* sp. (pH 5, adsorbent concentration = 0.1 g/30 mL, adsorbent size = 75 μm).

3.6. Pseudo-first order model

The possibility of adsorption data following Lagergren pseudo-first order kinetics is given by

$$\frac{dq}{dt} = K_1(q_e - q) \quad (3)$$

Integrating Eq. (3) with respect to integration conditions $q = 0$ to $q = q$ at $t = 0$ to $t = t$, the kinetic rate expression becomes:

$$\log(q_e - q) = \log q_e - \frac{K_1}{2.303}t \quad (4)$$

The pseudo first order rate constant K_1 can be obtained from the slope of plot between $\log(q_e - q)$ versus time, t . Fig. 6 shows the Lagergren pseudo-first order kinetic plot for the adsorption of copper onto *Ulva fasciata* sp. The pseudo first order rate constant K_1 values were calculated from the slope of Fig. 6. The calculated K_1 values and their corresponding linear regression correlation coefficient values are shown in Table 1. The linear regression correlation coefficient values R_1^2 found in the range

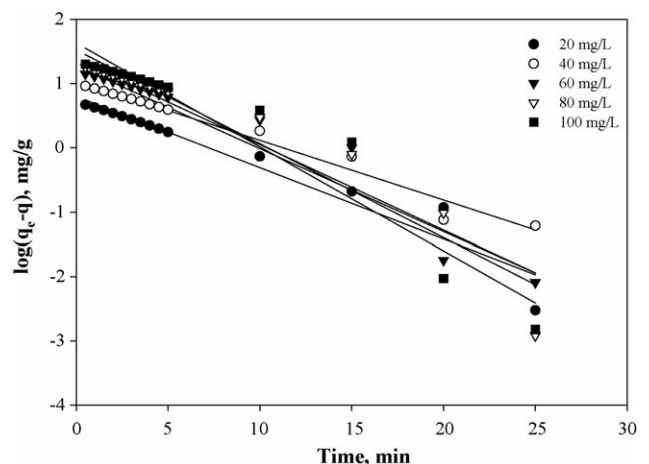


Fig. 6. Pseudo-first order kinetics for copper onto *Ulva fasciata* sp. (pH 5, adsorbent concentration = 0.1 g/30 mL, adsorbent size = 75 μm).

Table 1
Kinetic constants for copper onto *Ulva fasciata* sp

Initial concentration (mg/L)	Pseudo-first order constants (K_I)			Pseudo-second order constants (K_{II})		
	Rate constant (K_I)	Amount of copper adsorbed on adsorbent, q_e (mg/g)	Correlation coefficient (R_I^2)	Rate constant (K_{II})	Amount of copper adsorbed on adsorbent, q_e (mg/g)	Correlation coefficient (R_{II}^2)
20	0.2554	2.228	0.9377	0.0451	6.46	0.9982
40	0.2142	2.853	0.9749	0.0204	12.76	0.9979
60	0.3061	3.977	0.9416	0.0101	19.42	0.9968
80	0.3362	4.593	0.9226	0.0087	24.33	0.9966
100	0.3726	5.1269	0.9248	0.0072	27.62	0.9965

of 0.923–0.975, which shows that this model can be applied to predict the adsorption kinetic model.

3.7. Pseudo-second order model

A pseudo-second order model proposed by Ho and McKay [24] can be used to explain the adsorption kinetics. This model is based on the assumption the adsorption follows second order chemisorption. The pseudo-second order model can be expressed as:

$$\frac{dq}{dt} = K_{II}(q_e - q)^2 \quad (5)$$

Separating the variables in Eq. (5) gives:

$$\frac{dq}{(q_e - q)^2} = K_{II} dt \quad (6)$$

Integrating Eq. (6) for the boundary conditions $q=0$ to $q=q$ at $t=0$ to $t=t$, Eq. (6) simplifies to:

$$\frac{t}{q_t} = \frac{1}{K_{II}q_e^2} + \frac{1}{q_e}t \quad (7)$$

where t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time t . A plot between t/q_t versus t gives the value of the constant K_{II} (g/mg min) and q_e (mg/g) can be calculated (Fig. 7).

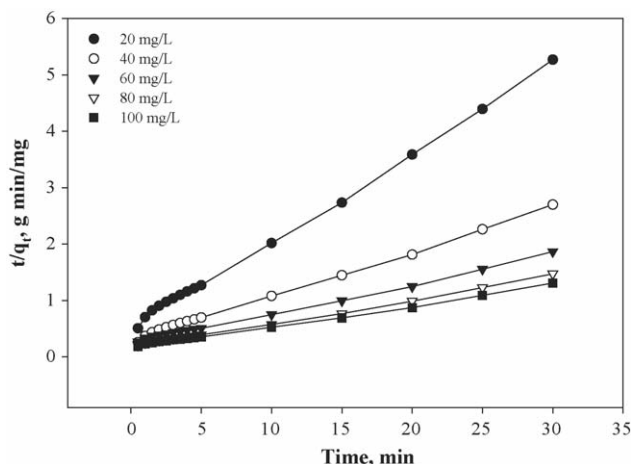


Fig. 7. Pseudo-second order kinetics for copper onto *Ulva fasciata* sp. (pH 5, adsorbent concentration = 0.1 g/30 mL, adsorbent size = 75 μ m).

The pseudo-second order rate constant K_{II} , the calculated q_e value and the corresponding linear regression correlation coefficient values R_{II}^2 are given in Table 1. At all initial copper concentrations, the linear regression correlation coefficient R_{II}^2 values were higher and ranged from 0.997 to 0.998. The higher R_{II}^2 values confirm that the adsorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the adsorption is due to chemisorption.

3.8. Adsorption equilibrium

The adsorption equilibrium defines the distribution of a solute phase between the liquid phases and solid phases after the adsorption reaction reached equilibrium condition. In the present study, equilibrium studies were carried out at room temperature 28 ± 2 °C. The equilibrium data were analysed using two of the most commonly used isotherm equations, Freundlich and Langmuir isotherm models.

The equilibrium data were very well represented by all the two equilibrium models (Fig. 8). The calculated isotherm constant at room temperature 28 ± 2 °C were given in Table 2. The best-fit equilibrium model was determined based on the linear regression correlation coefficient R^2 . From the table it was observed that the adsorption data were very well represented by Langmuir isotherm with an average higher correlation coef-

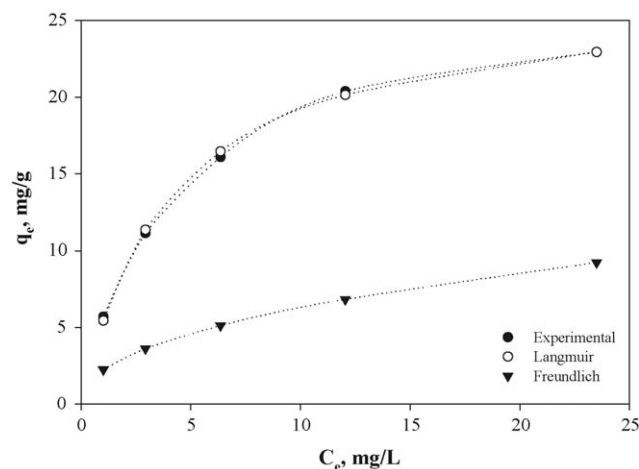


Fig. 8. Equilibrium curves for copper onto *Ulva fasciata* sp. (pH 5, initial metal concentration = 20 mg/L, adsorbent concentration = 0.1 g/30 mL, adsorbent size = 75 μ m).

Table 2
Equilibrium constants for copper onto *Ulva fasciata* sp.

Freundlich isotherm			Langmuir isotherm		
Adsorption capacity (K_F) (mg/g)	Adsorption intensity (n) (g/L)	Correlation coefficient (R^2)	Adsorption equilibrium constant (b) (L/mg)	Adsorption capacity, (q_e) (mg/g)	Correlation coefficient (R^2)
2.2230	0.4512	0.9606	0.2483	26.88	0.9995

Table 3
Comparison between the alga results of present study and others found in the literature

Adsorbent	Operation conditions				q_{\max} (mg/g)	Ref.
	pH	T ($^{\circ}\text{C}$)	C_0 (mg/L)	X (g/L)		
<i>Chlorella vulgaris</i>	4.5	25	100	1	40.0	[11]
<i>Scenedesmus obliquus</i>	4.5	25	100	1	20.0	[11]
<i>Synechocystis</i> sp.	4.5	25	100	1	23.4	[11]
<i>Chlorella fusca</i>	6	20	6.3	n.a. ^a	3.2	[15]
<i>Chlorella vulgaris</i>	4	25	100	0.75	37.6	[16]
<i>Chlorella vulgaris</i>	6	25	20	1	7.5	[25]
<i>Spirulina platensis</i>	6	25	20	1	10.0	[25]
<i>Chlorella vulgaris</i>	5	25	5	1	1.8	[26]
<i>Scenedesmus quadricauda</i>	4	25	5	1	2.8	[26]
<i>Saccharomyces cerevisiae</i>	5	25	100	0.1	1.25	[27]
<i>O. Limnetica</i>	4–5	25	1000	1	23.96	[28]
<i>A. Spiroides</i>	4–5	25	1000	1	0.2	[28]
<i>E. Elegans</i>	4–5	25	1000	1	1.08	[28]
<i>C. Vulgaris</i>	4–5	25	1000	1	9.47	[28]
<i>Ulva reticulata</i>	5.5		2000	0.2	74.63	[29]
<i>Manihot esculenta</i> Cranz	5	30	500	2.5	71.3	[30]
<i>Thuja orientalis</i>	7.7	16	50	4	19.23	[31]
<i>Ulva fasciata</i> sp.	5	28 \pm 2	100	0.1	26.88	Present study

^a n.a.: not available.

cient of 0.9995. The higher R^2 value for Langmuir isotherm confirms the approximation of equilibrium data to Henry's law at lower initial concentration. From Table 2, the Langmuir adsorption capacity q_e (mg/g) is 26.88 and the equilibrium constant b (l/mg) is 0.2483. The Freundlich constant K_F indicates the sorption capacity of the sorbent and the value of K_F is 2.223 mg/g. Furthermore, the value of ' n ' at equilibrium is 0.4512. It is noted that the value of ' n ' is smaller than 1, reflecting the unfavorable adsorption.

Table 3 shows a comparison between the results of this work and others found in the literature. The values of copper specific uptake found in this work were significantly higher than reported elsewhere. The comparison of sorption capacities of algae used in this study with those obtained in the literature shows that all the microorganisms are more effective for this purpose.

4. Conclusion

The biomass of the marine algae *Ulva fasciata* sp. demonstrated a good capacity of copper biosorption, highlighting its potential for effluent treatment processes. The kinetics of copper adsorption by inactive biomass of the marine algae *Ulva fasciata* sp. was fast, reaching 80% of the total adsorption capacity in 5 min. The adsorption process is a function of the adsorbent concentration, pH, metal ion concentration and adsorbent size.

Ulva fasciata sp. possesses a higher adsorption capacity of 26.88 mg/g, confirming that the algae under these conditions can be effectively used as adsorbent. The experimental data gave good fit with Langmuir isotherm and the adsorption coefficients agreed well with the conditions of favourable adsorption. Kinetic studies indicated that the adsorption tends to follow pseudo-second order kinetics for the range of concentrations studied for the entire adsorption period.

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