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The single batch biosorption of copper(II) ions on *Sargassum acinarum*

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ABSTRACT

In this study, the biosorption of copper(II) ions to *Sargassum acinarum*, a brown seaweed, was investigated in a batch system. The optimum biosorption conditions were determined as initial pH 5.5, temperature 25°C, initial copper(II) ion concentration 100 mg/L and biosorbent concentration 1.0 g/L. At the optimum biosorption conditions, the biosorption capacity of *S. acinarum* for copper(II) ions was found as 36.56 mg/g algae. The Langmuir and Freundlich isotherm models were applied to the biosorption data and the biosorption equilibrium was described well by the Langmuir isotherm model, with maximum biosorption capacity of 40.50 mg/g (0.637 mmol/g algae) of copper(II) ions. The intraparticle diffusion model and the pseudo-second-order kinetic model were applied to the experimental data in order to determine the removal mechanism and biosorption kinetic of copper(II) ions by *S. acinarum*. The pseudo-second-order kinetic model described very well the biosorption kinetic of copper(II) ions. Results showed that *S. acinarum* was an efficient biosorbent in the removal of copper(II) ions from an aqueous solution.

Keywords: Biosorption; Isotherm; Kinetic modelling; *Sargassum acinarum*; Copper(II)

1. Introduction

Many toxic heavy metals have been discharged into the environment with industrial waste waters, causing serious soil and water pollution and creating a major global concern [1]. Some metals such as copper, chromium, lead, mercury, manganese, cadmium, nickel, zinc, iron, platinum, silver, gold, ruthenium have toxic or harmful effects on many forms of life [2,3]. Various industries such as mining and smelting of metalliferous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leather working, photography, electric appliance manufacturing, metal surface treating, aero space and atomic energy installation etc. generate and discharge waste waters containing different heavy metals into the receiving waters [3–5]. The removal of toxic heavy metals from aqueous streams is an important problem for the various industries [6]. Many researchers have focused on removal of heavy metals from industrial waste waters using several conventional methods such as chemical precipitation, evaporation, membrane filtration, chemical coagulation and flocculation, ion exchange, adsorption, electrodialysis and reverse osmosis [3–7]. Major disadvantages of conventional

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treatment technologies are the production of toxic chemical sludge and other waste products and its treatment is a costly process and is not eco-friendly [8]. In addition, these techniques require expensive equipment and monitoring systems, need more chemical and energy. Also, these techniques are not preferred in industrial applications due to the low efficiency of purification. Biosorption is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity of biomass [9]. The major advantages of biosorption according to all of these conventional treatment methods are as follows [10]:

- Low cost, free availability and possible reuse of the biosorbent.
- High efficiency.
- Minimisation of chemical or biological sludge.
- The possibility of metal recovery.

Using large amounts of biosorbents, large amount of wastewaters can not only be purified, but microorganisms can be recovered as well. Recovery of microorganisms is referred to as desorption process. Metal ions received by micro-organisms can be recovered by solvent extraction. After heavy metals were removed from wastewaters by biosorption, the used biomass or waste sludge can be separated from the aqueous phase by filtration, drying and may be burned in incinerators to obtain energy and the heavy metals were recovered in the form of ash [11].

Biosorption is a biotechnological separation method that occurs naturally in certain biomass which binds contaminants onto its cellular structure. The biological materials used in biosorption are fungi, bacteria, yeast, moss, aquatic plants and algae [12]. Some types of biomass are very effective in removing heavy metals actually. The most important properties of an adsorbent for treatment processes are: capacity, selectivity, regenerability, kinetics, compatibility and cost [13]. Adsorbents can be selected from nature, industrial waste or rapidly growing micro-organisms. The most common industrial adsorbents are activated carbon, silica gel, and alumina, because they have great surface areas per unit weight [14]. Mango leaves [14], banana peel [15], crabshell [7,16], grapes talk [17], seaweed [18], neem leaf [19], palm kernel fibre [20], soursop seeds [21] are several low-cost and efficient biological materials which have been selected as adsorbent in recent studies.

In studies of heavy metals removal with biomass, dead (killed by heating, acid/base or chemical processes) and living cells were compared with the metal uptake capacities; it was observed that dead micro-organisms have higher metal uptake capacity. The reasons for this are listed below [22]:

- Any preventing metabolic event does not occur during the transportation of pollutants to the cell. So the biosorption process is not managed by physiological restrictions of microbial cells.
- The biosorption process including dead biomass is often faster as only cell surface-based binding, rather than active transport into the cell, occurs.
- Increase in permeability of the dead cell membrane.
- Changes in cell surface properties after the death of micro-organism.
- The use of dead biomass can prevent the problem of toxicity of heavy metals to living cells.
- Easy and non-destructive recovery of adsorbed metal ions, which allows regeneration of the biosorbent for reuse.

The phenomenon of heavy metal biosorption is not based on a single mechanism. Biosorption fundamentally involves adsorption process such as ionic, chemical and physical adsorption.

Biosorption of heavy metals from waste waters consists four steps [23]:

- In the first step, the metal is transported from the bulk solution to the boundary film surrounding the biosorbent.
- In the second step, the metal is transported from boundary film to surface of the biosorbent, through external diffusion.
- In the third step, the metal is transported from the surface to the intra-particle active sites, through internal diffusion.
- Finally, in the fourth step, uptake of metal at the active sites of biosorbent occurs, through various mechanisms including chemical reaction, physical binding or ion exchange.

Copper was chosen in this study with regard to its wide use in industry and potential pollution impact. Copper is a heavy metal commonly used in daily life and industry [24]. It is commonly used in construction, jewellery, dye, electrical and electronic, transportation, chemical industries. According to the US Environmental Protection Agency (EPA) and The World Health Organization (WHO), the permissible levels for copper in drinking water are 1.3 and $2\,\mathrm{mg\,dm^{-3}}$, respectively. High concentration levels of copper(II) ions in the industrial wastewaters must be reduced to acceptable levels before discharging them into the environment. *Sargassum acinarum*, brown algae, grown on Mediterranean Sea, was chosen as a biosorbent for the biosorption of copper(II) ions [25].

2. Materials and methods

2.1. Biosorbent

Sargassum acinarum, a kind of brown algae, was obtained from Mediterranean costs in Yumurtalık, Turkey. The algae was washed twice with tap water and dried in sunlight and then in an oven at 105℃ for 24 h. To obtain a stock biosorbent solution of 10 g/L, 10 g of inactivated algae was put in 1 L of distilled water and blended by using Waring Commercial Blender.

2.2. Copper(II) solution

One gram per litre of stock solution of copper(II) was prepared by dissolving weighed amount of $Cu(NO_3)_2$ in 1 L of distilled water. Necessary dilutions were made from the stock solution to prepare solutions in the range of initial copper(II) concentrations 20–200 mg/L. The initial pH of each solution was adjusted to the required value with concentrated and diluted H_2SO_4 and NaOH solutions before mixing the biosorbent suspension.

2.3. Batch studies

The biosorption experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL of biosorption solution. 10 mL of algae solution, except for the biosorbent concentration experiments, was contacted with 90 mL of metal bearing solution in an Erlenmeyer flask with a working volume of 100 mL at desired initial copper(II) concentration and then the flasks were agitated on a constant temperature and shaking rate for 120 min. Samples (3 mL) were taken before mixing the algae suspension and metal bearing solution and at pre-determined time intervals (0.5, 5, 10, 15, 20, 30, 60 and 120 min) for the residual metal ion concentration in the solution. Samples were centrifuged at 3,500 rev/min for 5 min, and the supernatant liquid was analysed at 460 nm wavelength with Chebios UV–VIS spectrophotometer. Experiments were repeated for different initial pH, initial copper(II) ion concentration, temperature and biosorbent concentration values. All of the experiments were carried out in duplicates and the average values were used in calculations.

2.4. Copper(II) analysis

The concentration of copper(II) ion remaining in the biosorption solution was determined spectrophotometrically, according to a previous report [26]. The maximum absorbance value for copper(II) ions was read at 460 nm. The copper(II) uptake amounts at equilibrium, q_{eq} (mg/g), were computed as follows:

$$q_{eq} = (C_0 - C_{eq})/X \qquad (1)$$

where C_0 and C_{eq} are the initial and equilibrium solute concentration (mg/L) and X is the biosorbent concentration in solution (g/L), respectively.

3. Results and discussion

Analysis of biosorption data is important for developing equilibrium and kinetics that can be used for design purposes. The biosorption of copper(II) ions on *S. acinarum* was investigated as a function of initial pH, initial solute concentration, temperature and biosorbent concentration.

3.1. The effect of initial pH

The initial pH is an important factor affecting the biosorption. pH is a parameter that affects the dissolution of metal, the activity of functional groups such as carboxyl, sulphate, phosphate, amino, etc. present on biosorbent and competition of metal ions.

The effect of initial pH on biosorption of copper(II) ions on *S. acinarum* was studied in the range of 3.0–5.5 at 100 mg/L initial copper(II) ion concentration, 25℃ temperature and 1 g/L biosorbent concentration for 60 min contact time. The variation of the biosorbed copper(II) amounts by *S. acinarum* with initial pH is given in Fig. 1. As seen from Fig. 1, the uptake

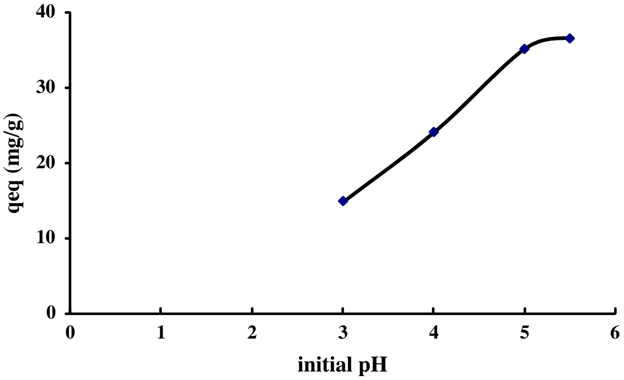

Fig. 1. The effect of initial pH (initial copper(II) concentration 100 mg/L, temperature 25℃, biosorbent concentration 1 g/L, agitation rate 200 rev/min).

amounts increased with increasing initial pH values and the optimum initial pH value was determined as 5.5. The percentage adsorption increased from 15.4 to 39.0% with an increase in solution pH from 3.0 to 5.5. The high uptake amount at high initial pH values is as a result of the electrostatic interaction between negatively charged surface of biosorbent and positively charged copper(II) ions. The increase in the initial solution pH will result in the increase of the dissociation degree of functional groups present on biosorbent surface, and in consequence, the number of electrostatic interactions will increase [27].

Proteins have an equal number of positive and negative charges at the isoelectric point. Algae cell surface has negative charge at pH above the isoelectric point, cell surface has positive charge at pH below the isoelectric point [28]. Hence, at lower pH values, hydronium ions [H_3O^+] compete with metal cations (Cu^{+2}) and this case reduces uptake capacity of algae for heavy metal ions. At higher pH values, metal cations can hold onto cell surface easily because of negatively charged of cell surface. Above pH 5.5–6.0, insoluble copper hydroxide starts precipitating from the solution, making true sorption studies impossible. As a result, the optimum pH for copper (II) biosorption was found as 5.5 and the other biosorption experiments were performed at this value.

3.2. The effect of temperature

One of the parameters affecting the biosorption is temperature. In order to determine the effect of temperature on copper(II) biosorption, the biosorption studies were carried out in the range of 20–50˚C temperature range and the variation of the biosorbed copper(II) amounts by *S. acinarum* with temperature is given in Fig. 2. The biosorption capacities and removal percents of *S. acinarum* decrease from 36.56 to 33.34 mg/g and from 39.0 to 36.0% with an increase in temperature from 25 to 50˚C, respectively. As can be seen from Fig. 2, the optimum biosorption temperature was found as 25˚C. The kinetic energy of the biosorbent particles increases with increasing temperature, so frequencies of collision increase and copper(II) ions are electrostatically adsorbed to the surface of biosorbent [29]. The surface activity of biosorbent reduces by increasing temperature and so the adsorbed metal ion amount at equilibrium decreases [30]. The reason for decrease in surface activity is decay of active regions on surface of the biosorbent at higher temperature or bond breaking. At higher temperature, the internal structure of micro-organisms may cause changes that affect the binding. The increase in copper (II) biosorption up to 25˚C can be explained with increase in active regions on the biosorbent surface or as a result of reduction in the thickness of the boundary layer surrounding the biosorbent with increase in temperature and decrease in mass transfer resistance for the solute [31]. The results show that an increase in the biosorption of copper(II) ions deals with an increase in the uptake capacity of *S. acinarum* with increasing temperature up to 25˚C.

3.3. The effect of initial copper(II) ion concentration

The effect of initial copper(II) ion concentration on biosorption was investigated between 25 and 300 mg/L of the initial copper(II) concentrations. The variation of the adsorbed copper(II) amounts per unit mass algae with initial copper(II) concentrations is presented in Fig. 3. The uptake amounts increased up to 100 mg/L of initial copper(II) concentration and did not change with further increase in initial copper(II) ion concentration, suggesting that available sites on the biosorbent are limiting factors for copper(II) biosorption. The uptake amounts increased with increasing initial metal

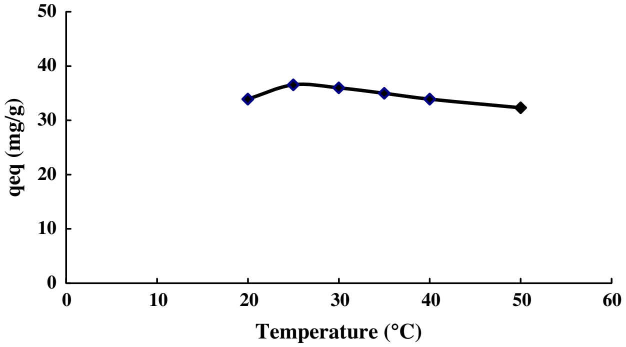

Fig. 2. The effect of temperature (initial copper(II) concentration 100 mg/L, initial pH 5.5, biosorbent concentration 1 g/L, agitation rate 200 rev/min).

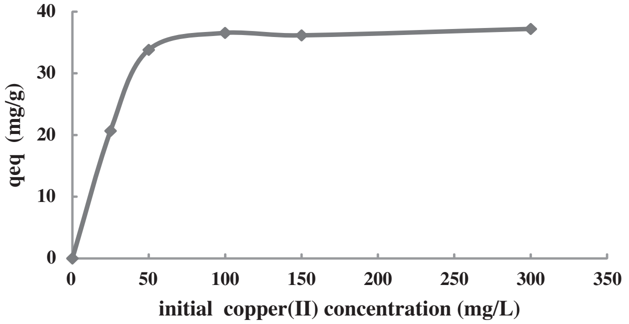

Fig. 3. The effect of initial copper(II) concentration (temperature 25˚C, initial pH 5.5, biosorbent concentration 1 g/L, agitation rate 200 rev/min).

ion concentration, as a result of the increase in the driving force. The uptake amounts were found as 16.45 mg/g for 25 mg/L and 36.56 mg/g for 100 mg/L initial copper(II) ion concentration. Removal yield decreased from 79.2 to 39.0%, with an increase in initial copper(II) ion concentration from 25 to 100 mg/L.

3.4. The effect of biosorbent concentration

Biosorption of copper(II) ions on *S. acinarum* was investigated at 0.5–3.0 g/L of biosorbent concentration range at initial pH 5.5, initial copper(II) ion concentration 100 mg/L and temperature 25°C. The variation of the copper(II) uptake amounts of *S. acinarum* with biosorbent concentrations is given in Fig. 4. The biosorbed copper(II) amount per unit mass algae decreased from 68.93 to 24.21 mg/g, while the copper (II) removal percent increased from 33.01 to 70.81%, with an increase in biosorbent concentration from 0.5 to 3.0 g/L, respectively. This observation can be explained by increase of the number of available adsorption sites with some increase in biosorbent concentration. On the contrary, the decrease in the biosorption capacity with increasing biosorbent concentration may be due to the particle interaction, such as aggregation, which would lead to a decrease in total surface area of the biosorbent and an increase in the diffusional path length. Accordingly, the optimum biosorbent concentration was determined as 1 g/L. As a result, the removal of a given amount of solute can be accomplished with greater economy of adsorbent if the solution is treated with separate small batches of adsorbent rather than in single batch, with filtration between each stage [32].

3.5. Equilibrium modelling

Equilibrium relationships between adsorbate and adsorbent are described by adsorption isotherm [33], usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. The Langmuir and Freundlich isotherm models are in common use for describing adsorption isotherms for water and wastewater treatment applications [30]. The Langmuir equation which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules is given by the following Eq. (2) [31]:

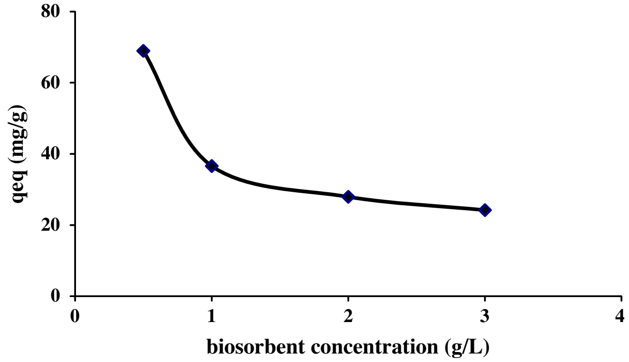

Fig. 4. The effect of biosorbent concentration (initial copper (II) concentration 100 mg/L, temperature 25°C, initial pH 5.5, agitation rate 200 rev/min).

$$q_{\mathrm{eq}} = [(Q^{\circ}\ b\ C_{\mathrm{eq}})/(1 + b\ C_{\mathrm{eq}})] \tag{2}$$

where q_{eq} (mg /g) and C_{eq} (mg/ L) are the adsorbed metal ion amount per unit mass of adsorbent and unadsorbed metal ion concentration, in solution at equilibrium, respectively. Q° and b are Langmuir constants related to maximum adsorption capacity and bonding energy of adsorption, respectively [30,31]. Q° and b can be determined form the linear plot of $1/q_{\mathrm{eq}}$ vs. $1/C_{\mathrm{eq}}$.

The empirical Freundlich equation that corresponds to the sorption on heterogeneous surface is given below [34] as follows:

$$q_{\mathrm{eq}} = K_{\mathrm{F}} \times C_{\mathrm{eq}}{}^{1/n} \tag{3}$$

where K_{F} and n are the Freundlich constants characteristic of the system. K_{F} and n are indicators of adsorption capacity and adsorption intensity, respectively. K_{F} and n can be determined form the linear plot of ln q_{eq} vs. ln C_{eq}. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.

The Langmuir and Freundlich isotherm models were applied to the equilibrium data of the biosorption of copper(II) ions on *S. acinarum* at different temperatures. The Q°, b, K_{F} and n values evaluated from the linearized Langmuir and Freundlich adsorption isotherms (data not shown) with regression coefficients for copper(II) biosorption are presented in Table 1.

According to Table 1, the isotherm constants (Q°, b, K_{F}) at 25°C, were higher than those for other temperatures. The maximum monolayer coverage capacity of algae (Q°) for copper(II) ions was determined as 40.5 mg/g (0.637 mmol/g algae) at 25°C which is the optimum temperature for biosorption of copper(II) ions to *S. acinarum*. q_{eq} values are found to be smaller than Q° indicating that the biosorption of copper(II) ions on *S. acinarum*.

As can be seen from Table 1, n values were greater than 1 at the studied temperatures indicating a high

Table 1
The Q°, b, K_F and n values evaluated from the isotherms at 25, 35 and 40°C temperatures with regression coefficients

	Langmuir isotherm			Freundlich isotherm		
Temperature (°C)	Q° (mg/g)	b (L/mg)	R^2	K_F	n	R^2
25	40.49	0.17	0.9981	16.41	5.83	0.8968
35	40.00	0.13	0.9727	13.31	4.53	0.7741
40	34.96	0.18	0.9462	12.94	4.72	0.9400

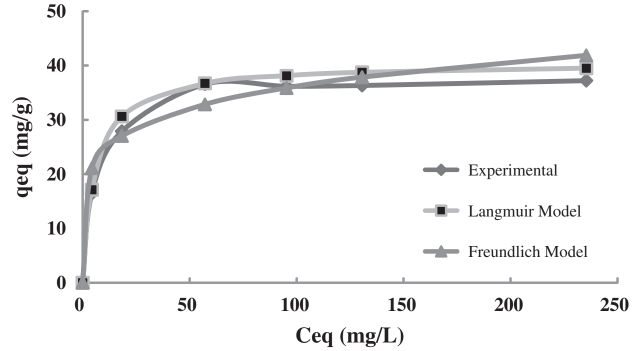

Fig. 5. Comparison of the experimental and predicted isotherms for copper(II) biosorption (temperature 25°C, initial pH 5.5, agitation rate 200 rev/min).

affinity of copper(II) ions to *S. acinarum*. Also, n values were very close to each other. So, the adsorption intensity was not affected by changing the temperature of adsorption solution [35].

The regression coefficients generated by the linear regression of each model were significantly high, but R^2 values obtained from Langmuir isotherm model were slightly higher than those of Freundlich isotherm model (Table 1). At 25°C and initial pH 5.5, the experimental and predicted isotherms for copper(II) biosorption were given in Fig. 5. From Fig. 5, the experimental data for copper(II) ions were in good agreement with those calculated by the Langmuir isotherm model.

A comparison of the maximum capacity, Q°, of *S. acinarum* with those some other biosorbents/adsorbents reported in literature is given in Table 2. The biosorption capacity of *S. acinarum* was relatively high when compared with other biosorbents. Differences of metal uptake are due to the properties of each biosorbent such as structure, functional groups and surface area.

Monolayer coverage of the surface by the metal ions can be used for the calculation of the specific surface area, S, according to following equation [43]:

$$S = [Q^\circ \times N \times A]/M \tag{4}$$

where S is the specific surface area, m^2/g algae; Q° is the monolayer coverage capacity of algae, mg metal/g algae; N is the Avogadro number, 6.02×10^{23}; A is the

Table 2
Comparison of the uptake capacities for copper(II) ions of various adsorbents/biosorbents

Adsorbent/biosorbent	Q°(mg/g adsorbent)	References
Sewage sludge ash (SSA)	4.1	[36]
Aureobasidium pullulans	6.0	[37]
Zeolite	6.7	[38]
Hevea brasiliensis	8.9	[39]
Melanin of Aureo basidium pullulans	9.0	[37]
Spent-grain	10.5	[40]
Agaricus bisporus	11.4	[41]
Cladosporium resinae	16.0	[37]
Sugar beet pulp	31.4	[42]
Sargassum acinarum	40.5	This study
Dehydrate wheat bran (DWB)	51.5	[43]
Entermorpha prolifera	57.1	[26]
Cladophora crispata	57.5	[35]
Spirogyra	133.3	[12]

cross-sectional area of metal ion, m^2; and M is the molecular weight of metal. The molecular weight and cross-sectional area of copper(II) are 63.5 g/g-mole and 1.58 $A^{\circ 2}$ in a close packed monolayer (copper(II) radius is 0.71 A°), respectively. The maximum surface area calculated from Eq. (4) for copper(II) biosorption on *S. acinarum* is 6.06 m^2/g algae. The maximum specific surface area of hazelnut shell and seed coat for copper(II) adsorption were determined as 0.62 m^2/g adsorbent and 1.123 m^2/g adsorbent, respectively [43,44]. This showed that the inactivated *S. acinarum* has a larger specific surface area than those for the hazelnut shell and seed coat.

3.6. Kinetic modelling

Implementing simple kinetic models, such as first- or second-order-kinetic models for sorption processes using solid surfaces is not generally true. Because, the processes containing solid surface are rarely homogeneous and it is difficult to distinguish transport phenomena and the effects of chemical reactions experimentally. For this reason; in order to determine the kinetics of metal sorption, studies have focused on the pseudo-second-order rate equation [43,45–47].

3.6.1. The pseudo-second-order kinetic model

The pseudo-second-order equation is based on the sorption capacity of the solid phase. This model predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step [30]. In order to quantify the extent of uptake in adsorption kinetics, a pseudo-second-order kinetic model can be used. The linear form of the pseudo-second-order kinetic model equation can be represented as follows [45]:

$$t/q_t = 1/k_2 q_{eq}^2 + t/q_{eq} \quad (5)$$

where k_2 is the the pseudo-second-order kinetic model rate constant (g/mg min), q_{eq} and q_t are the biosorbed copper(II) amount per unit mass of biosorbent at

Table 3
Comparison of the parameters obtained from the pseudo-second order kinetic model for copper(II) biosorption on *S. acinarum*

Initial pH	$q_{eq,exp}$ (mg/g algae)	$q_{eq,cal}$ (mg/g algae)	k_2 (g/mg min)	R^2
3.0	14.84	15.29	0.01853	0.9982
4.0	24.06	24.45	0.00795	0.9926
5.0	35.48	36.63	0.00695	0.9954
5.5	36.56	37.60	0.01040	0.9992
Initial copper(II) concentration (mg/L)	$q_{eq,exp}$	$q_{eq,cal}$	k_2	R^2
25	16.46	16.84	0.015307	0.9979
50	33.82	34.48	0.015318	0.9995
100	36.56	37.51	0.010452	0.9992
150	36.16	37.31	0.007706	0.9988
300	37.21	38.46	0.004630	0.9964
Temperature (°C)	$q_{eq,exp}$	$q_{eq,cal}$	k_2	R^2
20	33.90	35.34	0.00672	0.9974
25	36.56	37.59	0.01040	0.9992
30	36.00	36.49	0.02120	0.9998
35	35.00	36.10	0.00491	0.9912
40	33.90	34.60	0.01650	0.9990
50	32.34	32.68	0.03285	0.9997
Biosorbent concentration (g/L)	$q_{eq,exp}$	$q_{eq,cal}$	k_2	R^2
0.5	68.94	69.93	0.007805	0.9995
1.0	36.56	37.59	0.010400	0.9992
2.0	27.91	28.57	0.009562	0.9986
3.0	24.21	24.69	0.013433	0.9992

equilibrium and any time, t, respectively. If the pseudo-second-order kinetic model is applicable, the plot of t/q_t against t according to Eq. (5) should give a linear relationship, from which calculated $q_{eq,cal}$ and k_2 can be determined from the slope and intercept of the plot.

The pseudo-second-order kinetic model was applied to the biosorption data of copper(II) ions on *S. acinarum* at the different initial copper(II) ion concentrations, temperatures, initial pH and biosorbent concentrations and the rate constants; the experimental and calculated q_{eq} values and correlation coefficients are given in Table 3. The variations of experimental and calculated $q_t[q_t = (k_2\ t\ q_{eq}^2)/(1 + k_2\ t\ q_{eq})]$ values with time for different initial copper(II) ion concentrations and initial pH values are given in Figs. 6 and 7, respectively. As can be seen from Table 3, all correlation coefficients were very close to one and the experimental data ($q_{eq,exp}$) and the calculated values ($q_{eq,cal}$) were very close to each other. These results showed that the biosorption of copper(II) ions to *S. acinarum* was well described by the pseudo-second-order kinetic model.

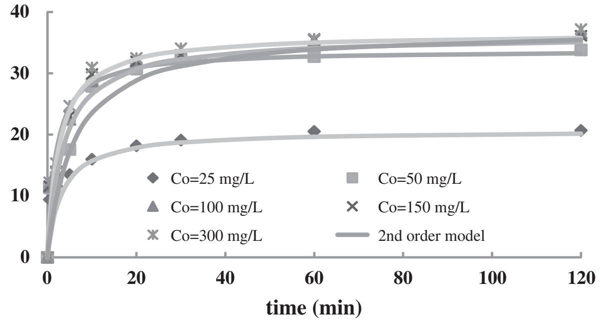

Fig. 6. Copper(II) uptake values by *S. acinarum* according to the pseudo-second order kinetic model at different initial copper(II) concentrations (temperature 25˚C, initial pH 5.5, agitation rate 200 rev/min).

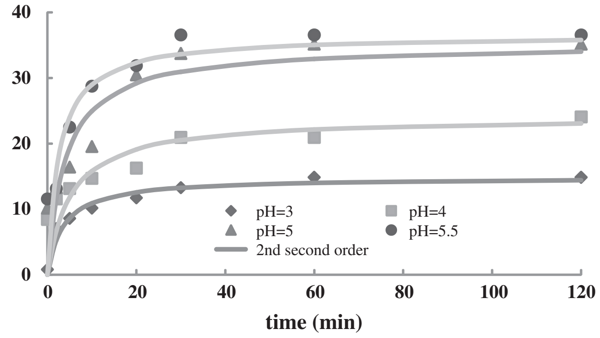

Fig. 7. Copper(II) uptake values by *S. acinarum* according to the pseudo-second order kinetic model at different initial pH values (temperature 25˚C, initial copper(II) concentration 100 mg/L, agitation rate 200 rev/min.).

One of the most important factors influencing the biosorption is the contact time. Figs. 6 and 7 show the variation of the biosorbed copper(II) amounts with contact time for the initial copper(II) ion concentrations and initial pH values, respectively. The data obtained from the biosorption of copper(II) ions on *S. acinarum* showed that a contact time of 60 min was sufficient to achieve equilibrium, and the biosorbed copper(II) amounts did not change with further increase in contact time for all of the studied concentrations and initial pH values.

3.6.2. Intra-particle diffusion model (Weber–Morris model)

The importance of external mass transfer greatly reduces for the process at very well-stirred batch system or system that the effect of stirring rate on equilibrium is insignificant. In a diffusion controlled adsorption process, the adsorbed amount of the solute varies almost proportionately with a function of retention time, $t^{1/2}$ as early mentioned by Weber and Morris [48]:

$$q_t = K_i \times t^{1/2} \tag{6}$$

According to this model, plot of uptake (q_t) vs. the square root of time should be linear if intraparticular diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step [49,50]. In many cases, an initial steep-sloped portion indicating external mass transfer is followed by a linear portion to the intraparticle diffusion and plateau which represents the final equilibrium stage, where the intraparticular diffusion starts to slow down due to extremely low solute concentration in the solution and surface.

Weber–Morris model was applied to the biosorption of copper(II) ions on *S. acinarum* as a function of the biosorbent concentration and the intraparticle diffusion model constants and regression coefficients are given in Table 4. As can be seen from Table 4, K_i values and intercepts decreased with increasing biosorbent concentrations and R^2 values are close to unity indicating the applicability of this model. The decreasing trend of intraparticle rate constant values with biosorbent concentrations was reported before by various investigators [26,50]. The observed decrease in K_i values with increasing biosorbent concentration may be due to agglomeration of biosorbent particles which leads to an increase in mass transfer resistance.

Table 4
The parameters obtained from Weber–Morris model for copper(II) biosorption

Biosorbent concentration (g/L)	K_i (mg/g min$^{1/2}$)	Intercept	R^2
0.5	7.23	29.51	0.9502
1.0	5.07	9.96	0.9601
2.0	2.76	9.82	0.9318
3.0	2.72	7.94	0.9335

It is also observed from Table 4 that, values of intercept give an idea about the thickness of the boundary layer, i.e. larger the intercept, greater is the boundary layer effect. As a result, mechanism of copper(II) removal on *S. acinarum* is complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate-determining step.

4. Conclusion

The biosorption of copper(II) ions to *S. acinarum* was studied in a batch system with respect to the initial pH, temperature, the initial copper(II) ion concentration and biosorbent concentration. The optimum biosorption conditions were determined to be initial pH 5.5, temperature 25℃, initial copper(II) ion concentration 100 mg/L and biosorbent concentration 1 g/L. At optimum biosorption conditions, the uptake amount and removal percentage of *S. acinarum* for copper(II) ions were found as 36.5 mg/g and 39.0%, respectively. The biosorption equilibrium was described well by the Langmuir isotherm model with maximum biosorption capacity of 40.50 mg/g (0.637 mmol/g algae) of copper(II) ions. The maximum specific surface area of *S. acinarum* for copper(II) biosorption was determined 6.06 m^2/g. The intraparticle diffusion model and the pseudo-second-order kinetic model were applied to the experimental data, in order to determine the removal mechanism and biosorption kinetic of copper(II) ions by *S. acinarum*. The pseudo-second-order kinetic model described very well the biosorption kinetic of copper(II) ions. As a consequence, inactivated *S. acinarum* is a good biosorbent for metal ions and has a high biosorption capacity, especially for copper(II) ions. The extraordinary potential for this natural, abundant and cheap seaweed can be used economically and successfully in selective removal of heavy metal ions from wastewaters.

Nomenclature

A	—	cross-sectional area of metal ion (m^2)
C_o	—	initial metal ion concentration (mg/L)
C_{eq}	—	residual metal ion concentration at equilibrium (mg/L)
k_2	—	pseudo-second-order rate constant (g/mg min)
K_F	—	adsorption capacity [(mg/g)(mg/L)$^{-1/n}$]
K_i	—	intraparticle rate constant (mg/g min$^{1/2}$)
M	—	molecular weight of metal (g/g-mole)
N	—	Avogadro number (6.02×10^{23})
q_{eq}	—	the amount of adsorbed metal ion per unit mass of biosorbent at equilibrium (mg/g)
$q_{eq,cal}$	—	calculated amount of adsorbed heavy metal per unit mass of biosorbent at equilibrium (mg/g)
$q_{eq,exp}$	—	experimental amount of adsorbed metal ion per unit mass of biosorbent at equilibrium (mg/g)
q_t	—	the amount of adsorbed metal ion per unit mass of biosorbent at any time (mg/g)
Q°	—	maximum adsorbed amount of metal ion per unit mass of biosorbent to form a complete monolayer on the surface bound at high C_{eq} (mg/g)
R	—	universal gas constant (8.314 J/mol K)
R^2	—	correlation coefficient
S	—	specific surface area (m^2/g algae)
T	—	absolute temperature (K)
X	—	the biosorbent concentration (g/L)
$1/n$	—	adsorption intensity

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