



## An eco-friendly process: Predictive modelling of copper adsorption from aqueous solution on *Spirulina platensis*

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### ABSTRACT

The adsorption of copper ions on *Spirulina platensis* was studied as a function of contact time, initial metal ion concentration, and initial pH regimes. Characterization of this adsorbent was confirmed by FTIR spectrum. Modified Gompertz and Logistic models have not been previously applied for the adsorption of copper. Logistic was the best model to describe experimental kinetic data. This adsorption could be explained by the intra-particle diffusion, which was composed of more than one sorption processes. Langmuir, Freundlich, and Redlich–Peterson were fitted to equilibrium data models. According to values of error functions and correlation coefficient, the Langmuir and Redlich–Peterson models were more appropriate to describe the adsorption of copper ions on *S. platensis*. The monolayer maximum adsorption capacity of copper ions was determined as  $67.93 \text{ mg g}^{-1}$ . Results indicated that this adsorbent had a great potential for removing of copper as an eco-friendly process.

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### 1. Introduction

Environmental contamination with heavy metals has increased throughout the world due to disposal of hazardous effluent into receiving waters [1,2]. Most industries such as automotive, electroplating, microelectronics, battery manufacture, metallurgical, etc., use metals, especially copper, which contribute to the increase of heavy metals in the water bodies [3,4]. Wastewater containing heavy metals causes a serious environmental problem [5,6]. Due to non-biodegradation of heavy metals, they accumulate in photosynthetic organisms and transfer pollutants to consumers, including humans [5,6].

Conventional methods like chemical precipitation, oxidation/reduction, ion exchange, reverse osmosis, and electrochemical treatment have been used for treating of wastewater contaminated with metal ions [1,4]. However, these methods are generally expensive and have a risk due to the possibility of generating hazardous by-products. Also, these processes produce large quantity of sludge that needs to be treated. Mehta and Gaur [1] reported that chemical precipitation and electrochemical treatment could be ineffective when applied for the removal of metal ion from dilute solutions, especially in the range of  $10\text{--}100 \text{ mg L}^{-1}$ . New eco-friendly and

cheap processes should be developed and adapted to reduce heavy metals concentrations to the allowable limits.

Biosorption has provided an alternative process to the traditional physico-chemical methods, utilizing inexpensive biomass to sequester toxic heavy metals [1,6,7]. In the last decades, many researchers have focus on the treatment of wastewater containing heavy metals by the use of living organisms and/or their biomass [1,4,8]. Many types of organisms such as bacteria, fungi, yeast, and algae or their biomasses, have been used for metal uptake [9,10]. Algal biomass is largely employed as an adsorbent material for several reasons. These are: (a) availability in large quantities, (b) largely cultivated throughout worldwide, (c) very effective adsorbent of heavy metals, and (d) relatively cheap for adsorption process [2,9]. In spite of the great number of studies related to the adsorption of heavy metals, this process has been studied at the laboratory-scale. Therefore, further research is necessary in order to apply this process for treatment of wastewater.

Cell walls of many organisms, including algae, consist of functional groups (such as amino, carboxyl, thiol, phosphoric, and sulphydryl) which are responsible for binding of metal ions [4]. Their intensity depends largely on the kind, number, affinity, and distribution on the cell wall. Therefore, the identification of functional groups is very important for understanding the mechanisms which are responsible for binding of certain metal ions.

Adsorptions of cationic materials are favored, when pH is higher than the zero point charge ( $\text{pH}_{\text{zpc}}$ ) of adsorbent. At this pH value, the adsorbent gets negatively charged due to electrostatic forces of

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### Nomenclature

$a_{R-P}$	Redlich–Peterson isotherm constant ( $L\text{mg}^{-1}$ ) <sup><math>\beta</math></sup>
$A$	maximum metal adsorption capacity from modified Gompertz and Logistic models ( $\text{mg g}^{-1}$ ).
$b$	Langmuir constant ( $L\text{mg}^{-1}$ )
$C_{\text{eq}}$	equilibrium metal concentration ( $\text{mg L}^{-1}$ )
$C_0$	initial metal concentration ( $\text{mg L}^{-1}$ )
$k$	pseudo second-order rate constant of adsorption ( $\text{g/mg min}^{-1}$ )
$K_F$	Freundlich adsorption capacity [ $(\text{mg g}^{-1})(\text{mg L}^{-1})^{-1/n}$ ]
$K_{R-P}$	Redlich–Peterson isotherm constant ( $L\text{mg}^{-1}$ )
$l$	intra-particle diffusion intercept ( $\text{mg L}^{-1}$ )
$M$	dry weight of biosorbent (g)
$n$	Freundlich adsorption intensity
$p$	significance level obtained from ANOVA
$\text{pH}_{\text{zpc}}$	the zero point charge of the adsorbent
$q_{\text{cal}}$	calculated amount of adsorbed metal per unit weight of biomass ( $\text{mg g}^{-1}$ )
$q_{\text{eq}}$	amount of adsorbed metal per unit weight of biomass at equilibrium ( $\text{mg g}^{-1}$ )
$q_{\text{exp}}$	experimental amount of adsorbed metal per unit weight of biomass ( $\text{mg g}^{-1}$ )
$q_0$	maximum metal adsorption capacity from Langmuir model ( $\text{mg g}^{-1}$ )
$q_t$	amount of adsorbed metal per unit weight of biomass at time $t$ ( $\text{mg g}^{-1}$ )
$R^2$	correlation coefficient
RSS	residuals sum of square
SSE	the sum of error square
$t$	time (min)
$V$	volume of the metal solution (L)
<i>Greek symbols</i>	
$\beta$	exponent in Redlich–Peterson isotherm
$\lambda$	lag time of adsorption for modified Gompertz and Logistic models (min)
$\mu$	adsorption rate for modified Gompertz and Logistic models ( $\text{min}^{-1}$ )
$\chi^2$	Chi-square test statistic

attraction. On the other hand, the adsorbent gets positively charged when pH value is lower than  $\text{pH}_{\text{zpc}}$  due to electronic repulsion [11–13].

Modelling of the adsorption data provides knowledge about the adsorption behavior and equilibrium state under environmental variables, such as pH regimes, material concentrations, temperature, ionic strength, etc. The Langmuir, Freundlich, and Redlich–Peterson are commonly used models for prediction of adsorption equilibrium, while pseudo second-order model is often applied to estimate adsorption kinetic process in the batch system [2,10,14]. Besides, several mathematical models such as the modified Gompertz and the Logistic, have been developed for describing the whole microbial growth curve [15,16]. The main advantages of these models provide more information about the system, such as the growth rate, the lag time, and maximum microbial growth.

In this study, copper (II) was selected as the target metal, since it is the one mainly found in wastewater due to its intensive use in industries. The objective of this study was the removal of copper ions from aqueous solution by dried biomass of *Spirulina platensis* as a function of contact time, initial metal concentration, and pH regimes in a batch system. The adsorption capacity of this adsorbent was predicted by use of the kinetic and equilibrium models.

The modified Gompertz and Logistic models, that have not been previously applied, were fitted to experimental data to get more information about the adsorption of copper ions. Furthermore, error functions were carried out to determine the best model.

## 2. Experimental

### 2.1. Preparation of adsorbent

The cyanobacterium used in the study, *S. platensis* [16] was inoculated on the Schlösser's medium [17]. This blue green alga was maintained in Erlenmeyer flasks placed on an orbital shaker at 90 rpm under 2.0 klux continuous illumination using cool, white fluorescent lamps. In the stationary state of growth [16], biomass of *S. platensis* was harvested by use of centrifugation at 6000 rpm for 6 min. After that pellet was washed twice with distilled water, centrifuged, and then dried at 70 °C for 24 h to obtain its dry biomass. After that, dried biomass was grinded and sieved through 75–100  $\mu\text{m}$  mesh, and stored in plastic bottles.

The zero point charge ( $\text{pH}_{\text{zpc}}$ ) of *S. platensis* was determined by using powder addition method [11,12]. A 0.5 g adsorbent and 50 mL 0.1 mol L<sup>-1</sup> NaCl solutions were mixed in 100 mL Erlenmeyer flask. Batch experiments were performed at various initial pH regimes ( $\text{pH}_i$ ), adjusted with 0.1 M HCl and/or 1.0 M NaOH solutions. Batches were agitated on shaker at 150 rpm for 24 h and the final pH ( $\text{pH}_f$ ) was measured at equilibrium. The value of  $\text{pH}_{\text{zpc}}$  was determined from the plot of  $\text{pH}_f$  against  $\text{pH}_i$ .

The infrared spectrum of nature and metal laden adsorbents were obtained by use of a Fourier transform infrared (FTIR) spectrometer (PerkinElmer Spectrum 100 FTIR Spectrometer) to identify the functional groups responsible for the adsorption.

### 2.2. Adsorbate

The metal solutions were prepared by diluting copper (II) stock solution ( $1\text{ g L}^{-1}$ ) in distilled water. Initial metal concentrations were adjusted to 25, 50, 75, 100, and 200  $\text{mg L}^{-1}$ , respectively, for the adsorption process. Copper was obtained from Sigma (Sigma–Aldrich GmbH, Germany).

### 2.3. Adsorption studies

The adsorption studies were carried out in 250 mL Erlenmeyer flask containing 100 mL of the adsorption solution. This adsorption solution consisted of 10 mL adsorbent suspension and 90 mL of metal solution at a known initial copper concentration, both at the desired pH (2–5). The adsorbent concentration in the final solutions was  $1.0\text{ g L}^{-1}$ . The pH of each solution was adjusted to the desired value with diluted or concentrated HCl and/or NaOH solutions before mixing the adsorbate or adsorbent suspension. The flasks were agitated on the orbital shaker at 150 rpm for 360 min, which was more than ample time for adsorption equilibrium.

Samples were taken at 0, 5, 10, 15, 30, 60, 120, 180, 240, 300, and 360 min. They were centrifuged at 6000 rpm for 5 min to precipitate the suspended adsorbent, and the supernatant liquid was analyzed for the residual concentration of metal ions using flame atomic adsorption spectrophotometer (PerkinElmer AA 400, USA) at the wavelength of 324.75 nm [5]. Experiments were repeated two times and average values are given in the present study. Blank experiments were conducted without the adsorbent.

The amount of copper ions per unit of adsorbent at time  $t$  ( $q_t$ ;  $\text{mg g}^{-1}$ ) and at equilibrium ( $q_{\text{eq}}$ ,  $\text{mg g}^{-1}$ ) were calculated by using Eq. (1) and Eq. (2), respectively,

$$q_t = \frac{(C_0 - C_t) \times V}{M} \quad (1)$$

$$q_{\text{eq}} = \frac{(C_0 - C_{\text{eq}}) \times V}{M} \quad (2)$$

where  $C_0$ ,  $C_t$ , and  $C_{\text{eq}}$  ( $\text{mg L}^{-1}$ ) represent concentrations of copper at initial, at  $t$  time, and at equilibrium in the solution, respectively.  $V$  is the volume of solution (L), and  $M$  is the mass of adsorbent (g).

#### 2.4. Adsorption kinetics

In order to investigate the adsorption kinetics of copper ions on *S. platensis*, the most commonly used pseudo second-order kinetic model (Table 1) was applied to experimental data.

The non-linear models such as the modified Gompertz and Logistic equations (Table 1) were fitted for the first time to experimental data, not only to describe the adsorption of copper ions on *S. platensis*, but also to reveal more information about the adsorption kinetics such as the adsorption rate ( $\mu$ ,  $\text{min}^{-1}$ ), the lag time of adsorption ( $\lambda$ , min), and the maximum metal uptake at equilibrium ( $A$ ,  $\text{mg g}^{-1}$ ).

The results of adsorption kinetics were also analyzed by the intra-particle diffusion model to identify the diffusion mechanism (Table 1).

#### 2.5. Equilibrium adsorption isotherms

Isotherms of Langmuir, Freundlich, and Redlich–Peterson (Table 1) were applied to describe the relationship between adsorbed copper ions per unit mass of *S. platensis* ( $q_{\text{eq}}$ ;  $\text{mg g}^{-1}$ ) and unadsorbed metal concentration in the solution ( $C_{\text{eq}}$ ;  $\text{mg L}^{-1}$ ) at the equilibrium.

The fitting procedure was performed by using the commercial computer software SigmaPlot version 11 (Systat Software, Inc., California, USA) via the Marquardt–Levenberg algorithm. This algorithm is used to minimize the sum of square of differences between experimental and predict data. In order to evaluate the goodness of fitting, correlation coefficients ( $R^2$ ) and error analyses [the sums of error squares (SSE), the residual sum of square (RSS) and Chi-square statistic ( $\chi^2$ )] (Table 1) were carried out between experimental and predicted data.

#### 2.6. Statistical analysis

Analysis of variance (ANOVA) was performed for the removal of metal ion concentration as a function of contact time, initial copper concentrations and pH regimes to determine significant differences using the SPSS version 16.0 (SPSS Inc., Chicago, IL, USA). Calculated parameters among factors were also compared using ANOVA.

### 3. Results and discussion

#### 3.1. Characterization of adsorbent

The metal adsorption capacity is strongly influenced from the surface structures of the adsorbent such as type and number of functional groups [25]. Functional groups of the adsorbent were determined by FTIR spectrometer. The FTIR spectrum of *S. platensis* showed several major intense bands, around 3265, 2908, 1642, 1396, and 1024  $\text{cm}^{-1}$  (Fig. 1). The peak at 3265  $\text{cm}^{-1}$  could be attributed to –OH and –NH groups [14,25,26]. Presence of –CH stretching vibrations could be confirmed by the adsorption peak at 2908  $\text{cm}^{-1}$  [12,25,27]. The adsorption peaks in the region 1730–1390  $\text{cm}^{-1}$  could be assigned to –C=O stretches aldehydes, ketones, and carboxylate [14,25]. In addition, –C–O, –C–C, and –C–OH stretching vibrations could be found at the adsorption peaks of the 1300–1000  $\text{cm}^{-1}$  region [25,28]. The adsorption peaks in the region 750–900  $\text{cm}^{-1}$  could be attributed to –P–O, –S–O, and aromatic –CH stretching vibrations [25,28]. The FTIR spectrum of the adsorbent indicated that copper ions could be bind to amino group and anionic groups due to electrostatic attraction. For example, amino (3265  $\text{cm}^{-1}$ ), carboxyl (1730–1390, 1300–1000  $\text{cm}^{-1}$ ), hydroxyl (3265, 1300–1000  $\text{cm}^{-1}$ ), and phosphate and sulphate (750–900  $\text{cm}^{-1}$ ) peaks areas were changed when adsorbent was loaded with copper (Fig. 1).

#### 3.2. Effect of initial pH regimes

The pH of the solution was one of the important factors governing the adsorption of copper ions. Initial pH regime has a critical role in metal adsorption by influencing the functional groups on the adsorbent surface and also the metal's solubility. The pH range

**Table 1**  
Equations of models and error functions.

	Equation and number	References
Kinetics models		
Pseudo second-order kinetics	$\frac{t}{q_t} = \frac{1}{k_2 q_{\text{eq}}^2} + \frac{t}{q_{\text{eq}}}$ (3)	[18]
Modified Gompertz	$y = A \exp \left[ -\exp \left\{ \left( \frac{\mu t}{A} \right) (\lambda - t) + 1 \right\} \right]$ (4)	[15]
Logistic	$y = \frac{a}{1 + (x/b)^c}$ (5) $\mu = \frac{-a}{4bc} (c + 1)^2 \left( \frac{c-1}{c+1} \right)^{c-1/c}$ $\lambda = b \left( \frac{c+1}{c-1} \right)^{c-1/c}$	[19]
Intra-particle diffusion	$q_t = k_1 t^{0.5} + I$ (6)	[20]
Equilibrium models		
Langmuir	$q_{\text{eq}} = \frac{b q_0 C_{\text{eq}}}{1 + b C_{\text{eq}}}$ (7)	[21]
Freundlich	$q_{\text{eq}} = K_F C_{\text{eq}}^{1/n}$ (8)	[22]
Redlich–Peterson	$q_{\text{eq}} = \frac{K_R - p C_{\text{eq}}}{1 + q_R - p C_{\text{eq}}}$ (9)	[23]
Error function		
Chi-square statistic	$\chi^2 = \sum_{i=1}^m \left[ \frac{(q_{\text{exp}} - q_{\text{cal}})^2}{q_{\text{cal}}} \right]$ (10)	[12]
The sums of error squares	$\text{SSE} = \sqrt{\sum \frac{(q_{\text{exp}} - q_{\text{cal}})^2}{N}}$ (11)	[24]
Residuals sum of square	$\text{RSS} = \sum (q_{\text{cal}} - q_{\text{exp}})^2$ (12)	[15]

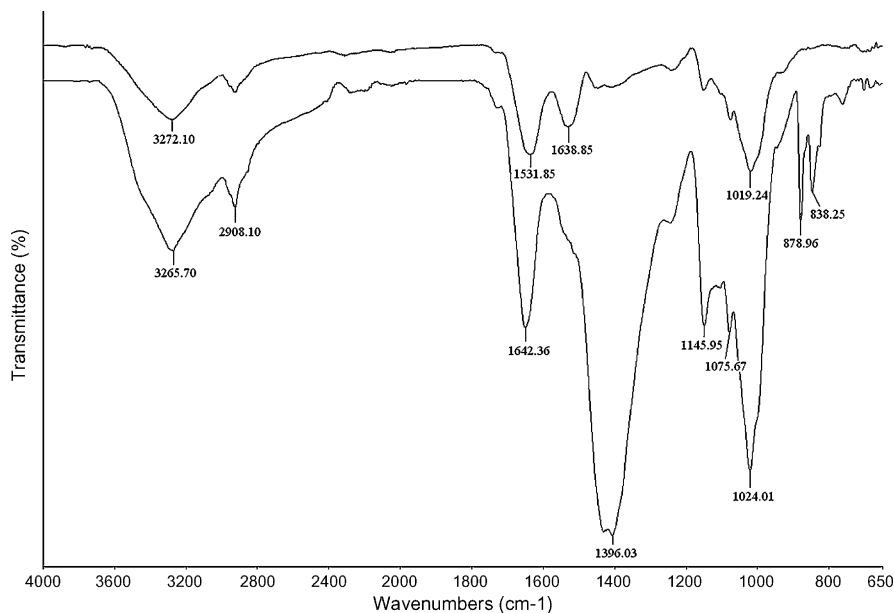


Fig. 1. FTIR spectra of *Spirulina platensis*.

of solutions was adjusted to 2–5 because copper ions precipitated as  $\text{Cu}(\text{OH})_2$  in a solution with a pH value above 6 [5,29,30].

The effect of pH for the adsorption of copper ions on *S. platensis* is given in Fig. 2. The initial pH values strongly affected ( $p < 0.01$ ) the adsorption of copper ions. At a pH value of 2, the metal adsorption by the cyanobacterium was found to be the lowest. At this pH high concentration of  $\text{H}^+$  ions could be very effective in excluding metal ions from binding to the sites on cell surface. Similar results were also reported in literature for the adsorption of copper on different adsorbents [4,5,27].

The zero point charge ( $\text{pH}_{\text{zpc}}$ ) of the adsorbent is one way to understand the adsorption mechanisms [11,13]. The  $\text{pH}_{\text{zpc}}$  of *S. platensis* was found as pH 8.5, where electrostatic repulsion between adsorbent molecules is at minimum. When pH of the solution is lower than that of  $\text{pH}_{\text{zpc}}$  values, the surface of the adsorbent gets positively charged. This limits the adsorption capacity of metal

ions due to electrostatic repulsion. The amount of adsorbed metal at pH 2 was found to be lower than that at pH 5 because the surface of the adsorbent get more positively charged at the lower pH [5,29,31,32]. Decreasing the pH of the solution causes to increase in positively charged (protons) group density on the surface of the adsorbent, and electrostatic repulsion occurs between metal ions and functional groups on the surface. Therefore, adsorption capacity of biomass reduced with decreasing the pH of the solution.

### 3.3. Adsorption kinetic of copper ions

The adsorption of copper ions on *S. platensis* as a function of contact time and initial metal concentrations with predicted data from pseudo second and Logistic models are shown in Figs. 3 and 4, respectively. The adsorption of this metal ( $q_t$ ,  $\text{mg g}^{-1}$ ) increased ( $p < 0.01$ ) with increasing contact time. Rapid adsorption was

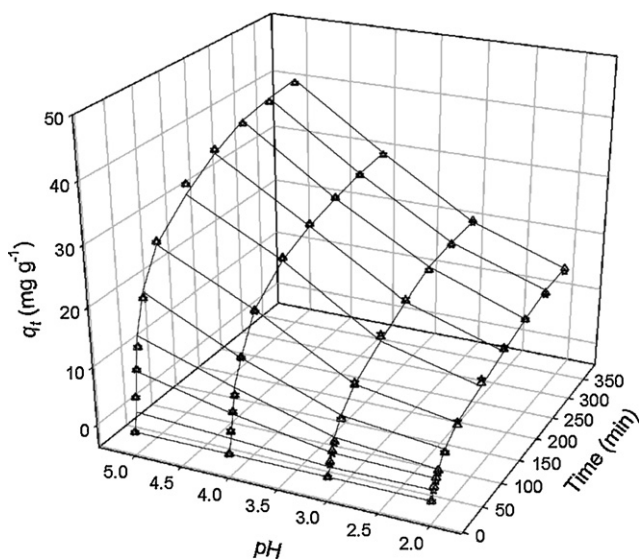


Fig. 2. Effects of initial pH regimes and contact time on the adsorption of copper ions on *Spirulina platensis* at  $100 \text{ mg L}^{-1}$ . Mesh lines show experimental kinetic data. Symbols of triangle and star exhibit the predicted data from Logistic and pseudo second-order models, respectively.

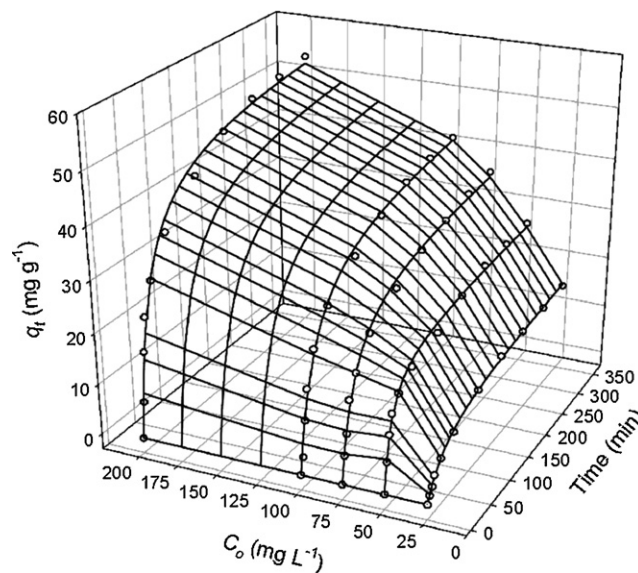


Fig. 3. Effects of initial metal concentrations and contact time on the adsorption of copper ions on *Spirulina platensis* at pH 5. Comparison between the experimental points and fitted curves by pseudo second-order kinetic model.

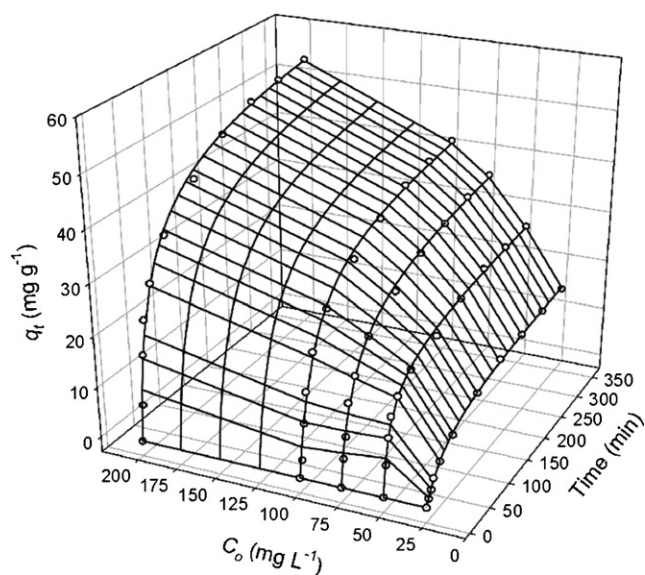


Fig. 4. Comparison between the experimental points and fitted curves by Logistic model as a function of initial metal concentrations and contact time on the adsorption of copper ions on *Spirulina platensis* at pH 5.

observed during the first 60 min of contact time. Thereafter, the increment rate of copper adsorption reduced until the equilibrium state. About 300 min of contact time was sufficient to achieve this state and further increase in contact time did not change significantly ( $p > 0.05$ ) the adsorption of copper ions (Figs. 3 and 4). Similar results were also found in previous studies [2,8,24,28].

A change in the initial copper concentration from 25 to 200 mg L<sup>-1</sup> caused an increase in the amount of adsorbed metal value from 13.74 to 52.63 mg g<sup>-1</sup> (Figs. 3 and 4). This could be due to an increase in the driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases. These results were also reported in previous studies [5,24,33].

Pseudo second-order and intra-particle diffusion models were applied to experimental data in order to investigate the adsorption kinetics. Additionally, non-linear models like the modified Gompertz and Logistic equations [15,16,19] were also fitted to

experimental data, not only to describe the adsorption of copper ions on *S. platensis*, but also to reveal more information about the adsorption kinetics, such as the adsorption rate ( $\mu$ ; min<sup>-1</sup>), lag time ( $\lambda$ ; min) and maximum metal uptake at equilibrium ( $A$ ; mg g<sup>-1</sup>).

The values of  $k$  and  $q_{cal}$  determined from pseudo second-order kinetic model are given in Table 2. High values of  $k$  suggested that copper ions could be removed rapidly with this adsorbent. Besides,  $q_{cal}$  values agreed well with the  $q_{exp}$  (experimental) values having a high correlation coefficient (shown in Fig. 3). The straight-line of  $t/q_t$  against  $t$  plots (not shown) indicated the ability of this model to describe the experimental kinetic data. As a result, it could be stated that adsorption of copper ions support the assumption of chemisorption [18]. Similar results were also found in literature [14,24,31,34].

The modified Gompertz and Logistic models have not been previously fitted to experimental kinetic data in order to describe the adsorption of copper ions on *S. platensis*. Results given in Table 2 showed that the modified Gompertz model had remarkable correlation coefficient ( $R^2 > 0.93$ ). However, these correlation coefficients were lower than those of the Logistic model. According to the values of  $R^2$  ( $\geq 0.986$ ) and RSS (0.25–22.73), the Logistic was found to be the most suitable model to describe the adsorption of copper ions on *S. platensis* (Table 2). Moreover, predicted  $q_t$  values from the Logistic equation agreed very well with the experimental  $q_t$  values (Fig. 4).

Adsorption rates ( $\mu$ ) determined from the modified Gompertz and Logistic models increased with the increasing initial copper concentration in the solution as it was expected (Table 2). However, there was no correlation between the adsorption rate determined from pseudo second-order kinetic and the initial copper concentration of the solution (Table 2). Adsorption rates of modified Gompertz and Logistic models were found to be higher at pH 5 than at pH 2. The relationships between pH and adsorption rates from pseudo second-order kinetics were not observed. These results indicated that the modified Gompertz and Logistic models were more appropriate to describe the adsorption of copper ions on *S. platensis* than that of pseudo second-order model.

Maximum metal uptake at equilibrium,  $q_{cal}$  for pseudo second-order model and  $A$  for the modified Gompertz and Logistic models, are given in Table 2. Maximum metal uptake increased with increasing the initial metal concentration and pH regimes. Maxi-

Table 2  
Kinetic parameters for the adsorption of copper ions on *Spirulina platensis* ( $t = 360$  min,  $M = 1$  g L<sup>-1</sup>).

$C_o$	pH	$q_{exp}$	Pseudo second-order kinetic				Modified Gompertz				Logistic			
			$q_{cal}$	$k$	$R^2$	RSS	$A$	$\mu$	$R^2$	RSS	$A$	$\mu$	$R^2$	RSS
25 mg L <sup>-1</sup>	2	5.45	5.908	0.0049	0.993	0.2830	5.091	0.0657	0.954	1.8341	6.221	0.169	0.994	0.2507
	3	6.76	7.581	0.0031	0.994	0.4241	6.489	0.0637	0.964	2.3219	8.176	0.179	0.995	0.3369
	4	10.50	11.132	0.0027	0.981	2.8401	9.828	0.0997	0.931	9.7756	13.194	0.335	0.986	2.0619
	5	13.74	15.906	0.0013	0.997	0.9617	13.315	0.1413	0.978	6.2323	15.670	0.303	0.997	0.9410
50 mg L <sup>-1</sup>	2	7.69	8.300	0.0029	0.988	0.9979	7.124	0.0673	0.948	4.1184	9.463	0.197	0.990	0.7663
	3	12.83	13.685	0.0027	0.994	1.4594	11.895	0.2405	0.969	7.7052	13.192	0.396	0.994	1.2603
	4	19.62	20.460	0.0029	0.985	7.5665	18.224	0.6740	0.969	15.4155	19.238	0.821	0.991	4.5180
	5	25.44	25.701	0.0026	0.987	9.5783	23.221	0.6744	0.931	50.0404	27.501	1.702	0.989	7.6899
75 mg L <sup>-1</sup>	2	11.42	12.762	0.0019	0.993	1.3744	10.638	0.1612	0.972	5.4022	11.884	0.235	0.995	0.9363
	3	17.59	18.789	0.0022	0.993	2.9869	16.469	0.3791	0.973	11.5404	17.686	0.553	0.997	1.3653
	4	23.87	25.626	0.0012	0.996	3.3613	21.987	0.352	0.965	27.6434	25.346	0.709	0.996	3.3213
	5	34.74	36.271	0.0010	0.993	11.1737	31.871	0.4935	0.951	74.5032	38.549	1.318	0.994	9.1644
100 mg L <sup>-1</sup>	2	14.70	12.762	0.0011	0.987	3.7323	13.829	0.0942	0.951	14.0239	22.667	0.295	0.994	1.5810
	3	20.23	18.789	0.0065	0.993	7.5772	19.370	0.1396	0.964	21.2162	27.325	0.365	0.995	2.7628
	4	29.93	25.626	0.0076	0.997	3.2966	27.865	0.3712	0.971	37.2439	32.376	0.721	0.997	3.7969
	5	40.52	36.271	0.0069	0.993	15.7298	37.482	0.5736	0.957	97.9508	43.571	1.270	0.993	15.7225
200 mg L <sup>-1</sup>	2	20.80	21.884	0.0012	0.977	12.1945	19.595	0.1374	0.935	34.3941	34.060	0.557	0.992	4.4915
	3	30.10	32.584	0.0007	0.989	13.3197	28.125	0.2380	0.950	58.7175	40.697	0.755	0.995	6.0736
	4	38.78	44.173	0.0004	0.986	28.6947	37.353	0.2240	0.958	84.7398	65.477	0.706	0.995	10.8665
	5	52.63	55.064	0.0001	0.991	30.6867	48.744	0.6969	0.946	190.5811	59.753	1.938	0.994	22.7261

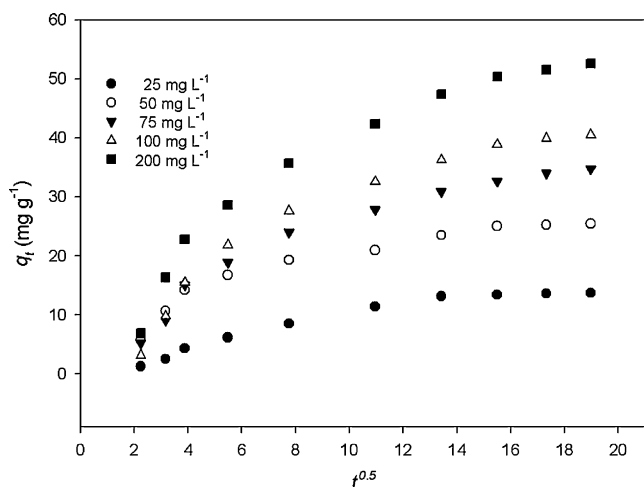


Fig. 5. Intra-particle diffusion model for the removal of copper ions on *Spirulina platensis* at pH 5.

imum copper adsorption capacity of *S. platensis* was calculated from the Logistic model as  $65.477 \text{ mg g}^{-1}$ , which was higher than those of mentioned kinetic models (Table 2).

Lag time ( $\lambda$ ; min) determined from the modified Gompertz and Logistic models are not given in Table 2, because they had negative values. It can be stated that no adaptation time was required for the adsorption of copper ions, because these are readily adsorbed on *S. platensis*. These results could also be observed in figures of previous adsorption studies [7,10,30].

The adsorption results were further evaluated by using the intra-particle diffusion model (Fig. 5) to explain the diffusion mechanism [20]. Weber and Morris [20] stated that if a linear regression exists between  $q_t$  and  $t^{0.5}$ , intra-particle diffusion is the sole rate limiting step. However, if multi-linear plots are observed, it can be concluded that two or more steps are present in the adsorption process. Fig. 5 shows that the plots were not linear over the whole time of the study. Therefore, more than one process was present, such as surface adsorption and intra-particle diffusion. At the beginning of the adsorption the rate of copper removal was very fast due to external surface adsorption, but after this initial phase the intra-particle diffusion occurs and limits the rate of adsorption. Increment rate of diffusion reduced at the equilibrium state due to the consequence of decreasing of copper ions ( $C_{eq}$ ,  $\text{mg L}^{-1}$ ). Similar results were also observed in literature [2,32].

### 3.4. Equilibrium modeling

The isotherms of Langmuir, Freundlich, and Redlich–Peterson (Table 1) were fitted to describe the equilibrium data between adsorbed material on the adsorbent ( $q_{eq}$ ;  $\text{mg g}^{-1}$ ) and unadsorbed pollutant in solution ( $C_{eq}$ ;  $\text{mg L}^{-1}$ ). The values of parameters, correlation coefficients and results of error functions are summarized in Table 3.

Langmuir parameters,  $q_0$  and  $b$ , were found to be higher at pH 5 than those of other pH regimes. As can be seen in Table 3, the maximum copper adsorption capacity of *S. platensis* was calculated from Langmuir model as  $67.93 \text{ mg g}^{-1}$ , which was closer to the result of the Logistic model. A comparison of the maximum copper adsorption capacity reported for various algal species is given in Table 4. Results of the present study indicated that *S. platensis* showed remarkable potential for the removal of copper ions from aqueous solution when compared with other algal adsorbents (Table 4). This could be due to difference on the surface properties of each adsorbent such as functional groups, surface area, particle size, dosage, etc.

Table 3

pH dependence of the isotherm parameters and results of error functions for the removal of copper ions on *Spirulina platensis* ( $t = 360 \text{ min}$ ,  $C_0 = 25\text{--}250 \text{ mg L}^{-1}$ ,  $M = 1 \text{ g L}^{-1}$ ).

Isotherms		pH 2	pH 3	pH 4	pH 5
Langmuir	$q_0$	37.20	49.38	52.41	67.93
	$b$	0.0071	0.0091	0.0178	0.0243
	$R^2$	0.986	0.997	0.992	0.997
	$\chi^2$	0.31017	0.06413	0.16569	0.14301
	SSE	0.65010	0.42521	0.83398	0.77414
	RSS	2.11313	0.90403	3.47764	2.99649
Freundlich	$K_F$	0.8867	1.538	3.8332	6.4928
	$n$	1.6354	1.7166	2.1650	2.3390
	$R^2$	0.981	0.983	0.961	0.944
	$\chi^2$	0.25367	0.46254	0.96291	1.93737
	SSE	0.75397	1.00604	1.88404	3.12376
	RSS	2.84234	5.0605	17.7480	48.7893
Redlich–Peterson	$K_{R-P}$	0.2797	0.4497	0.8989	1.4001
	$a_{R-P}$	0.0115	0.0091	0.0143	0.0093
	$\beta$	0.9254	1.0005	1.0338	1.151
	$R^2$	0.986	0.997	0.992	0.999
	$\chi^2$	0.28771	0.06406	0.15938	0.02514
	SSE	0.64902	0.42519	0.82845	0.38412
RSS	2.10612	0.90394	3.43163	0.73776	

Symbols of isotherm parameters are given in Nomenclature section.

The constants of the Freundlich isotherm,  $K_F$  and  $n$ , ranged 0.887–6.493 and 1.635–2.339, respectively. High values of these parameters at pH 5 showed easy separation of copper ions from aqueous solution.

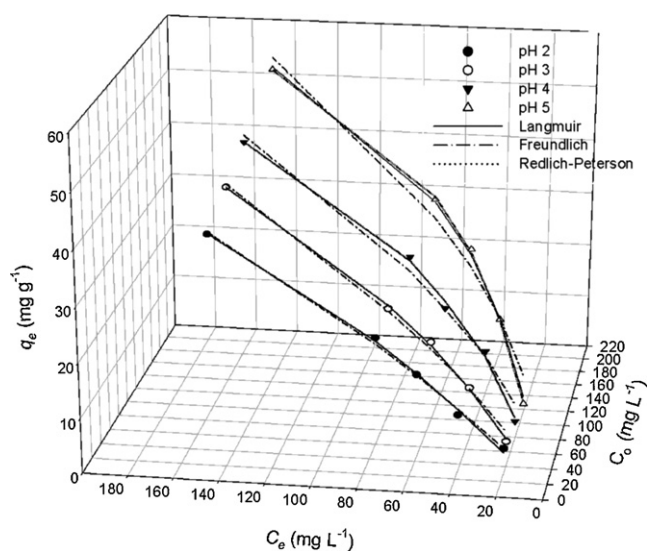
Values of  $K_{R-P}$  and  $\beta$  obtained from Redlich–Peterson isotherm increased with increasing pH of solution from 2 to 5. Since, the  $\beta$  values were found to be equal to 1 (Table 3), the Redlich–Peterson equation converts to the Langmuir form [23]. Adsorption is more heterogeneous, when  $\beta$  equals to  $[1 - (1/n)]$  [13]. However, significant difference ( $p < 0.05$ ) was observed between values of  $\beta$  and results of  $[1 - (1/n)]$ . Therefore, it could be stated that the adsorption of copper ions could not be heterogeneous.

In Fig. 6 (plots of  $q_{eq}$  vs.  $C_{eq}$ ) the applicability of the Langmuir, Freundlich and Redlich–Peterson models is showed. The experimental data were fitted to the aforementioned models and had high correlation coefficients. However, correlation coefficients of the Langmuir and Redlich–Peterson isotherms were higher than those of the Freundlich model (Table 3). Besides, the values of the sums of error squares (SSE), the residual sum of square (RSS) and Chi-square statistic ( $\chi^2$ ) were found to be lower for Redlich–Peterson, and the Langmuir models (Table 4), in agreement with the findings of Liu et al. [7]. So, it could be concluded that both models were well fitted to the experimental data, while Freundlich isotherm gave poor fitting according to values of  $R^2$  and the error functions. Besides, values of  $\beta$  from Redlich–Peterson isotherm attributed to the suitability of

Table 4

Adsorption capacities of copper ions by various algal adsorbent ( $C_0$ ,  $\text{mg L}^{-1}$ ;  $M$ ,  $\text{g L}^{-1}$ ;  $q_{max}$ ,  $\text{mg g}^{-1}$ ).

Adsorbent	pH	$C_0$	$M$	$q_{max}$	References
<i>Turbinaria ornata</i>	6	1000	2.0	147.06	[3]
<i>Laminaria japonica</i>	5–6	254.2	1.0	108.04	[7]
<i>Spirulina platensis</i>	5	200	1.0	67.93	This study
<i>S. platensis</i>	6	20	1.0	10.38	[35]
<i>Scenedesmus quadricauda</i>	5	600	n.a	75.60	[32]
<i>Scenedesmus obliquus</i>	4.5	100	1.0	20.00	[36]
<i>Chlorella vulgaris</i>	5	250	0.1	58.80	[30]
<i>C. vulgaris</i>	4.5	100	1.0	40.00	[36]
<i>Enteromorpha prolifera</i>	4	200	1.0	57.14	[33]
<i>Gelidium</i> sp.	5.3	317.8	0.4	31.14	[27]
<i>Ulva fasciata</i> sp.	5	100	0.1	26.88	[5]
<i>Synechocystis</i> sp.	4.5	100	1.0	24.00	[36]
<i>Oscillatoria limnetica</i>	4–5	1000	1.0	23.96	[36]



**Fig. 6.** Comparison of the experimental and predicted data from Langmuir, Freundlich and Redlich–Peterson models for the adsorption of copper ions on *Spirulina platensis*.

Langmuir model for the adsorption of copper ions on *S. platensis*. Therefore, it could be stated that its adsorption could be based on the assumption of the Langmuir model that maximum adsorption is related to a saturated monolayer of adsorbate molecules on the adsorbent surface [21]. The suitability of the Langmuir isotherm was also observed in previous adsorption studies [24,26,31,32].

#### 4. Conclusion

The adsorption of copper ions on *S. platensis* was affected by contact time, initial metal concentration, and pH regime. The adsorption kinetics was well described by the Logistic model, and had a good correlation between adsorption rates and initial copper ion concentration or pH regimes. Results of intra-particle diffusion indicated that more than one process could be present during the adsorption. The maximum adsorption capacity was found by the Langmuir isotherm as  $67.93 \text{ mg g}^{-1}$  with high values of  $R^2$  and low values of error functions. Consequently, this adsorbent has a great potential for removing of copper from aqueous solution as an eco-friendly process.

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