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Kinetic and equilibrium studies on the adsorption of reactive red 120 from aqueous solution on *Spirogyra majuscula*

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ABSTRACT

The removal of reactive red (RR) 120 on *Spirogyra majuscula* was performed as a function of initial dye concentration, contact time and pH regimes. Change in pH values strongly affected ($p < 0.01$) the adsorption of RR 120 and increasing initial pH value decreased the amount of adsorbed dye. Amount of dye uptake increased ($p < 0.01$) with increasing contact time and concentration of initial dye. Adsorption behavior was well described by pseudo second-order kinetic model. It was observed that equilibrium dye uptake significantly increased ($p < 0.01$) from 25.52 to 351.97 mg g^{-1} when initial RR 120 concentration increased from 25 to 750 mg L^{-1}. Experimental data were well fitted to Langmuir, Freundlich and Redlich-Peterson models. Three different error functions were conducted to find better model to describe the experimental data. The lower values of error functions exhibited that Freundlich model was more suitable for the adsorption of RR 120, which implied a heterogeneous sorption phenomenon. Results indicated that *S. majuscula* could be used as adsorbent in industrial scale for textiles wastewater treatment without excessive cost.

1. Introduction

Dye and dyestuffs are extensively used in various industries such as textile, plastic, food, cosmetic, carpet and paper [1–3]. Wastewaters of these industries containing dye with metals, salts, etc. which may be toxic and even carcinogenic for aquatic life. Charges of such wastewater into receiving waters cause to damage ecological balance on affecting photosynthetic activity due to reduction of light penetration [1,4]. Hence, the presence of dyes in wastewaters is one of the major environmental problems. They can be removed from wastewater because dyes and pigments are visible pollutant even at low concentrations [2].

More than 100,000 dyes are commercially available and most of them are difficult to decolorize because of their complex structure and synthetic origin [3,5]. Moreover, degradation of dyes is more difficult, because they are specifically designed to resist fading upon exposure to light, sweat and water.

Presence of color in dye bearing effluents is one of the complex environmental problems. Removal of dye in wastewater has been made by physical, physico-chemical, biological and/or chemical processes [3,5,6]. Activated carbon is the most commonly used method for the treatment of dye bearing wastewaters. However, this method can be uneconomic due to high cost of activated carbon [2,7,8].

The use of biomaterials for the treatment of wastewaters provides as an alternative method to the conventional treatment. These biosorbents have many advantages over conventional treatments that are economic, nontoxic to environment and widespread [2,9,10]. A wide variety of microorganisms such as fungi, algae and bacteria either in their living or inactivated biomass form has been investigated to remove dyes from wastewaters [5,11,12]. Adsorption on algae has been mainly attributed by the functional groups on the cell wall, which consist of various chemical groups such as carboxyl, hydroxyl, amino, phosphate [2,6,13]. Each algal species, has distinctive cell wall properties, has been proved to be effective biosorbent for the treatment of wastewaters [7,12,15].

Reactive red dye has anionic characteristics and contains some functional groups such as hydroxylates, sulfonates, and chloride [7]. In the present investigation, biomass of *Spirogyra majuscula* was selected to remove reactive red (RR) 120 from aqueous solutions. *S. majuscula* is a filamentous green alga growing and widespread in aquatic ecosystems such as creeks, lakes, ponds and pools [14]. Objective of the present study, were to examine the potential of a widespread freshwater alga *S. majuscula* for the removal of commonly used dye, RR 120, in textile industry and to determine equilibrium and kinetic parameters for RR 120 in a batch system as a function of initial dye concentration and pH regimes.

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Nomenclature

$a_{R\text{-}P}$	Redlich-Peterson isotherm constant $(L\,mg)^{\beta}$
b	Langmuir constant (L mg)
β	exponent in Redlich-Peterson isotherm
C_{eq}	equilibrium dye concentration ($mg\,L^{-1}$)
C_0	initial dye concentration ($mg\,L^{-1}$)
k_1	pseudo first-order rate constant of sorption ($L\,min^{-1}$)
k_2	pseudo second-order rate constant of sorption ($g\,mg\,min^{-1}$)
K_F	Freundlich adsorption capacity ($(mg\,g^{-1})(mg\,L^{-1})^{-1/n}$)
$K_{R\text{-}P}$	Redlich-Peterson isotherm constant (L mg)
n	Freundlich adsorption intensity
q_{eq}	amount of adsorbed dye per unit weight of biomass at equilibrium ($mg\,g^{-1}$)
q_{exp}	experimental amount of adsorbed at equilibrium ($mg\,g^{-1}$)
q_{cal}	calculated amount of adsorbed at equilibrium for pseudo first- and second-order models ($mg\,g^{-1}$)
q_o	maximum amount of the dye per unit of biomass to form a complete the monolayer adsorption capacity ($mg\,g^{-1}$)
q_t	amount of the dye per unit of biomass at time t ($mg\,g^{-1}$)
RR	reactive red
R^2	correlation coefficient
t	time (h)
V	volume of the dye solution (L)
M	dry weight of biosorbent (g)
p	significance level obtained from ANOVA
MPSD	The Marquardt's percent standard deviation error function
ARE	the average relative error
ARS	the average relative standard error
m	number of data points
r	number of parameter

2. Materials and methods

2.1. Algal biomass

The alga used in the study, *S. majuscula* was obtained from a freshwater pool in University of Gaziantep. The species was filamentous green alga and appeared as an elongated filament composed of cylindrical cells. The species had spiral chloroplast, end cell wall plane, conjugation tubes occurred from both gametangia, and lens-shaped smooth zygospore [14].

S. majuscula was collected from littoral site of the pool, washed twice with tap water in order to remove adhering larvae of organisms, soil, etc. After that, it was dried in an oven at 80 °C for 24 h. Powder of this alga was obtained by grinding and sieving (100–75 μm mesh sizes) of dried biomass.

The zero point charge (pH_{zpc}) of *S. majuscula* was determined by using powder addition method. A 0.5 g adsorbent and 50 mL NaCl solutions were mixed in 100 mL Erlenmeyer. Two sets of batch experiments were carried out with 0.1 and 0.01 M NaCl solutions. Initial pH regimes (pH_i) were adjusted by 0.1 M HCl and 1 M NaOH solutions. Batches were agitated on the shaker at 150 rpm for 24 h of contact time. After that, final pH (pH_f) was measured, the value of pH_{zpc} could be determined from the plot of pH_f against pH_i (Fig. 1) [16,17].

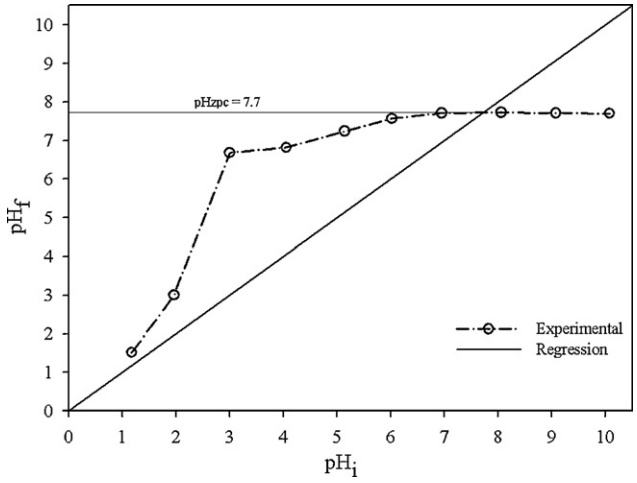

Fig. 1. Determination of zero point of charge (pH_{zpc}) of *Spirogyra majuscula*.

The infrared spectra of nature and dye laden adsorbents were analyzed using a Fourier transform infrared (FTIR) spectrum (PerkinElmer Spectrum 100 FTIR Spectrometer) to identify the functional groups responsible for the adsorption.

2.2. Batch experiments

Reactive red (RR) 120 (Procion Red HE-3B; $C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$) was obtained from Sigma (Sigma–Aldrich Chemical Co., St. Louis, USA). The chemical structure and properties of RR 120 is given in Fig. 2 and Table 1. Stock dye solution was prepared in distilled water as $1.0\,g\,L^{-1}$. For the adsorption studies, the adsorbent suspension was prepared by using this algal powder.

Adsorption studies were performed in 250 mL Erlenmayer flask containing 100 mL of adsorption solution (10 mL adsorbent suspension and 90 mL adsorbate at known concentration). Ten milliliters adsorbent suspension having desired pH (2, 3, 4 or 5) and 90 mL of dye solution at known initial dye concentration having desired pH (2, 3, 4 or 5) were mixed in an Erlenmeyer flask. The pH of each solution was adjusted to required value with diluted or concentrated HCl and NaOH solutions before mixing the adsorbate or adsorbent suspension. The initial dye concentrations were adjusted to 25, 50, 75, 100, 150, 300 and 750 $mg\,L^{-1}$. The value of adsorbent in the final solutions was $1.0\,g\,L^{-1}$. These flasks were agitated on the orbital shaker at 150 rpm for 48 h to ensure equilibrium.

Samples (5 mL) were taken before mixing of adsorbent suspension with dye bearing solution, then at time intervals (0.083, 0.17, 0.25, 0.5, 1.0, 2.0, 3.0, 24.0, 48.0 h) for the determination of residual dye concentration. After that, samples were centrifuged to precipitate suspended biomass at 5000 rpm for 5 min. The concentration of dye in the supernatant was determined by spectrophotometer (Jenway 6305) at 515 nm. Duplicates experiments were carried out and used data in the present study were the mean values of two replicate determinations.

Amount of RR 120 uptake per unit mass of adsorbent at time t (q_t, $mg\,g^{-1}$) and at equilibrium (q_{eq}, $mg\,g^{-1}$) were calculated by

Table 1
The general characteristics of RR 120.

Name of dyes	Procion Red HE-3B
Chemical formula	$C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$
Molar mass	1469.98
Color index name	Reactive red 120
CAS number	61951-82-4
λ_{max} (nm)	515

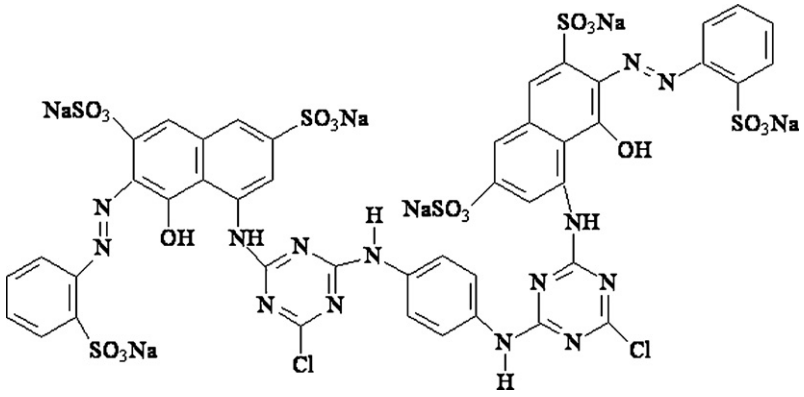

Fig. 2. The chemical structure of RR 120.

using Eqs. (1) and (2), respectively.

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

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

where C_0, C_t and C_{eq} represent at initial, at t time and at equilibrium concentrations of RR 120 (mg L^{-1}) in the solution, respectively. V is the volume of solution (L), and M is the mass of adsorbent (g).

2.3. Statistical analyses

Analysis of variance (ANOVA) was performed for amount of removal of dye as function of initial pH regimes and initial dye concentrations to determine significant difference using the SPSS version 15.0 (SPSS Inc., Chicago, IL, USA). The fitting procedure was performed using commercial computer software SigmaPlot version 11 (Systat Software, Inc., California, USA) via the Marquardt–Levenberg algorithm. Tukey's Honestly Significant Difference (HSD) multiple range test was also carried out to distinguish examined groups.

3. Results and discussion

The removal of RR 120 on *S. majuscula* was performed as a function of initial dye concentrations and initial pH regimes.

The peak at 3278 cm^{-1} could be attributed to –OH and –NH_2 groups [3,18,19]. The peaks at 2929 and 1648 cm^{-1} may be attributed to –C–H alkane stretches and –C=O stretches aldehydes, ketones, carboxylic acid, respectively [18,19]. The band at 1408 could be assigned as amid or sulfamide groups [18]. The adsorption peaks at 1033 and 872 cm^{-1} could be attributed to –C–O stretches and aromatic –CH stretching vibrations, respectively [18,19]. The FTIR spectrum of adsorbent indicated that RR 120 molecules were bounded with the presence of amine and amide groups, which were responsible functional groups, in agreement with finding of Arıca and Bayramoğlu [7].

3.1. Effect of initial pH regimes

pH is one of the most important environmental factors in the adsorption studies due to its influence on the site dissociation and the chemistry of dye in solution. Therefore, pH regimes cause to change not only adsorption availability and speciation of dyes, but also the adsorption capacity [10,16].

The effect of pH regimes on the adsorption of RR 120 on *S. majuscula* at initial dye concentration of 100 mg L^{-1} is given in Fig. 3. Change in pH values strongly affected ($p < 0.01$) the adsorption of RR 120 and increasing initial pH value decreased the amount of adsorbed dye at the equilibrium state (Fig. 3).

Effect of pH on the dye uptake could be explained on the basis of zero point charge (pH_{zpc}) of the biosorbent [8,16,17]. The pHzpc of *S. majuscula* was determined as pH 7.7 (Fig. 1), where electrostatic repulsion between adsorbent molecules is a minimum. When pH is lower than pH_{zpc}, the surface of the adsorbent gets positively charged, which absorbing more dye due to electrostatic force of attraction. The surface of the adsorbent is negatively charged, when pH is higher than pH_{zpc} causing to decrease capacity of adsorption due to electronic repulsion. It was reported that electrostatic attraction could be essential mechanism in the adsorption of pollutants on the alga [16,17]. However, Aksu and Tezer [20] stated that it could be very difficult to explain the adsorption mechanism with respect to pH. It could be due to a large number of variables involved in the adsorption of dye such as the number and type of functional groups on the adsorbent surface, water chemistry, etc. Furthermore, the wastewaters containing dye has higher salt concentration due to consuming large amount of salts in dyeing processes. Thus, ionic strength or salinity concentration could be affected the adsorption capacity of adsorbent for removing dye [2,7,8,17].

3.2. Effect of initial dye concentration

Initial dye concentrations provide an important driving force to overcome all mass transfer resistance of dye between the aqueous and solid phases [10,15]. The adsorption of RR 120 on *S. majuscula* at different initial dye concentrations is shown in Fig. 4. It

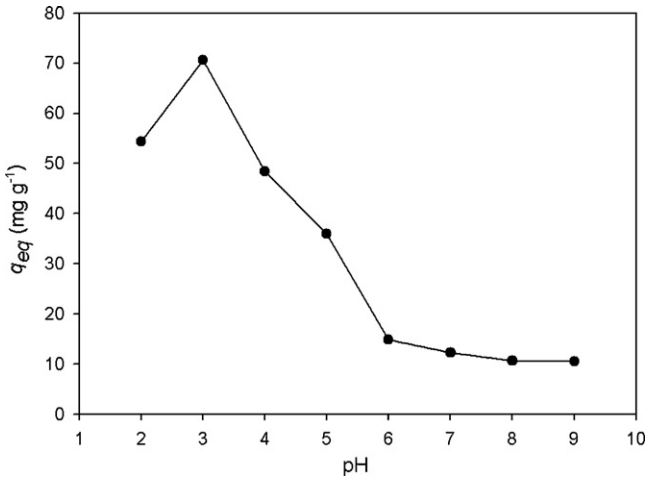

Fig. 3. The effect of pH regimes on the adsorption of RR 120 on *Spirogyra majuscula* at initial dye concentration of 100 mg L^{-1}.

Table 2
Pseudo first- and second-order rate constants at initial dye concentrations and pH regimes.

C_0	pH	q_{exp}	Pseudo first kinetic			Pseudo second kinetic		
			k_1	q_{cal}	R^2	k_2	q_{cal}	R^2
25	2	23.65	0.2085	21.42	0.965	0.0173	22.31	0.981
	3	24.52	0.1317	23.36	0.959	0.0086	24.60	0.991
	4	21.20	0.3438	18.85	0.945	0.0355	19.55	0.970
	5	15.14	0.0228	13.31	0.858	0.0023	14.36	0.941
50	2	33.48	0.0752	30.79	0.939	0.0033	32.81	0.982
	3	45.95	0.1152	39.92	0.872	0.0040	42.51	0.945
	4	28.93	0.1054	27.07	0.955	0.0060	28.47	0.989
	5	23.20	0.0370	18.82	0.769	0.0022	20.88	0.886
75	2	47.58	0.0661	40.11	0.882	0.0019	43.66	0.954
	3	61.94	0.1813	55.12	0.927	0.0051	58.03	0.965
	4	38.51	0.1871	35.09	0.937	0.0089	36.75	0.984
	5	27.68	0.1516	21.08	0.734	0.0086	22.76	0.821
100	2	54.44	0.2127	46.81	0.877	0.0068	49.47	0.939
	3	70.68	0.1513	57.87	0.796	0.0034	62.02	0.889
	4	48.39	0.1044	42.22	0.874	0.0034	45.06	0.951
	5	35.94	0.0931	31.01	0.906	0.0037	33.39	0.956
150	2	86.05	0.1366	72.27	0.884	0.0026	76.99	0.939
	3	105.72	0.0997	86.82	0.860	0.0010	93.57	0.922
	4	70.88	0.1354	56.95	0.833	0.0030	61.12	0.904
	5	49.62	0.1654	42.01	0.889	0.0057	44.51	0.944
300	2	153.52	0.0314	130.52	0.857	0.0003	143.29	0.944
	3	215.15	0.0225	189.96	0.898	0.0002	206.49	0.966
	4	115.67	0.0626	98.06	0.858	0.0007	107.05	0.941
	5	75.88	0.1533	69.44	0.978	0.0036	72.66	0.984
750	2	223.14	0.0314	130.52	0.997	0.0010	230.16	0.987
	3	351.97	0.0225	189.96	0.994	0.0012	358.74	0.992
	4	121.83	0.0626	98.06	0.991	0.0008	126.82	0.993
	5	93.45	0.1533	69.44	0.903	0.0010	97.76	0.901

was observed that increasing initial dye concentration significantly increased ($p < 0.01$) the uptake of RR 120 on the algal adsorbent. These results were also in agreement with previous studies for different microorganisms such as *Caulerpa scalpelliformis* for basic yellow dye [10], *Chlorella vulgaris* for reactive dyes [20].

It was observed that a large amount of RR 120 was rapidly removed by dried biomass of *S. majuscula* during the first 1.5 h contact time. After then, rate of removal of dyes slowed down gradually until the equilibrium state. The removal of higher dye concentrations needed longer contact time ($p < 0.01$) than those of lower dye concentration (Fig. 4). Similar results were also found in previous studies [15,20,21].

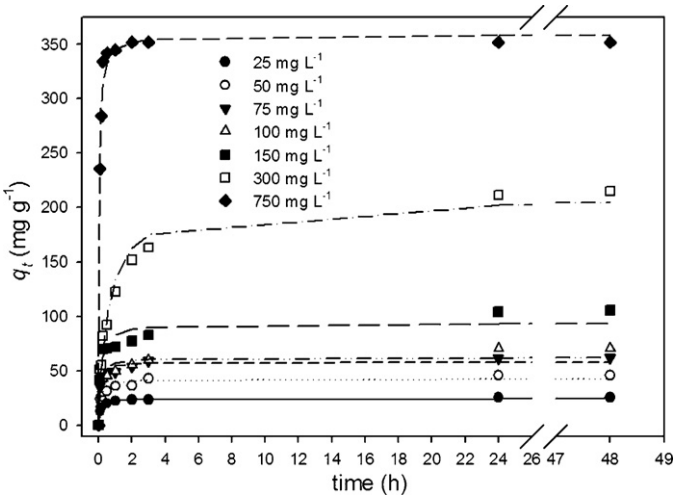

Fig. 4. Effects of initial dye concentrations and contact time on RR 120 uptake on *Spirogyra majuscula* at pH 3. Lines on the plot show predicted q_t values from pseudo second-order kinetic model.

3.3. Kinetic modeling

The passive uptake of pollutants such as dye and metals from aqueous solutions by use of non-living microbial mass is called adsorption [2,10]. The prediction of batch adsorption kinetics provides the most important information for designing adsorption systems [5]. Adsorption kinetics includes the search for a best model that well represents the experiment data as function of environmental conditions.

In the present study, pseudo first- and second-order kinetic models were applied to describe the adsorption of RR 120 on *S. majuscula* as function of initial dye concentrations, contact time and pH regimes.

The pseudo first-order Lagergren equation [22] is given as

$$\frac{dq}{dt} = k_1(q_{eq} - q_t) \tag{3}$$

where q_{eq} and q_t (mg g^{-1}) are the amount of adsorbed dye on the adsorbent at equilibrium and at time t. k_1 is the rate constant of pseudo first-order kinetic model. For applying boundary conditions $t = 0$ to t and $q = 0$ to q_t the integrated form of Eq. (3) leads to:

$$\log(q_{eq} - q_t) = \log\ q_{eq} - \frac{k_1}{2.303}t \tag{4}$$

The parameters and correlation coefficients of pseudo first-order kinetic model for the adsorption of RR 120 were determined from non-linear regression by using a commercial software of SigmaPlot version 11 via the Marquardt–Levenberg algorithm are summarized in Table 2. The values of the adsorption rate constant, k_1, can also be determined from the plot of $\log(q_{eq} - q_t)$ *vs* t. It was

Table 3
Parameters of Langmuir, Freundlich and Redlich-Peterson models for the adsorption of RR 120 on *Spirogyra majuscula*.

pH	Langmuir model				Freundlich model			Redlich-Peterson model			
	q_o	$b \times 10^{-3}$	R_L	R^2	K_F	n	R^2	$K_{R\text{-}P}$	$a_{R\text{-}P}$	β	R^2
2	333.0076	3.9648	0.25166	0.976	6.7239	1.7749	0.968	74.1619	10.6534	0.4412	0.968
3	722.4399	2.3629	0.36073	0.984	5.4156	1.4339	0.986	69.6350	12.3114	0.3077	0.986
4	156.0759	7.3318	0.15387	0.955	8.8345	2.3772	0.901	62.5305	6.8245	0.5846	0.907
5	123.1965	4.8798	0.21460	0.980	4.2996	2.0799	0.968	49.8661	11.3288	0.5224	0.969

Non-linear regression was carried out for Langmuir, Freundlich and Redlich-Peterson models.

not suitable to describe the whole adsorption process of RR 120 on *S. majuscula*. The first state, initial 30 min of contact time, of the adsorption of RR 120 could be only described by pseudo first-order kinetic model [23].

The pseudo second-order model is related with the sorption capacity of adsorbent [23]. The pseudo second-order kinetic model is represented as:

$$\frac{dq_t}{dt} = k_2(q_{eq} - q_t)^2 \quad (5)$$

where k_2 is the pseudo second-order rate constant (g mg min^{-1}). For boundary conditions $t = 0$ to t and $q = 0$ to q_t the integrated form of Eq. (5) leads to:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \quad (6)$$

The parameters (k_1 and q_{cal}) obtained from pseudo second-order kinetic model, correlation coefficient, R^2 and experimental q_{exp} are given in Table 2. The values of pseudo second model parameters, q_{eq} and k_2, can also be determined from slope and intercept of t/q_t *vs* t plot (Fig. 5). There was an inverse relationship observed between the pseudo second-order rate constant k_2 and initial dye concentrations values (Table 2). These results also observed in previous adsorption studies [5,17,21,24]. The high values of k_2 suggested that RR 120 could be removed rapidly on *S. majuscula*, in agreement with findings of Punjongharn et al. [8]. From Table 2, there was no significant differences ($p > 0.05$) between experimental and predicted q_{eq} values from pseudo second-order model.

Experimental and predicted q_t values from pseudo second kinetic against time (t) are given in Fig. 4. Pseudo second-order kinetic model with high R^2 values exhibited well fitting to experimental data, in agreement with findings of Özer et al. [9] and Han et al. [25]. Pseudo second-order kinetic model could be regarded as sufficient to describe the adsorption of RR 120 on *S. majuscula*.

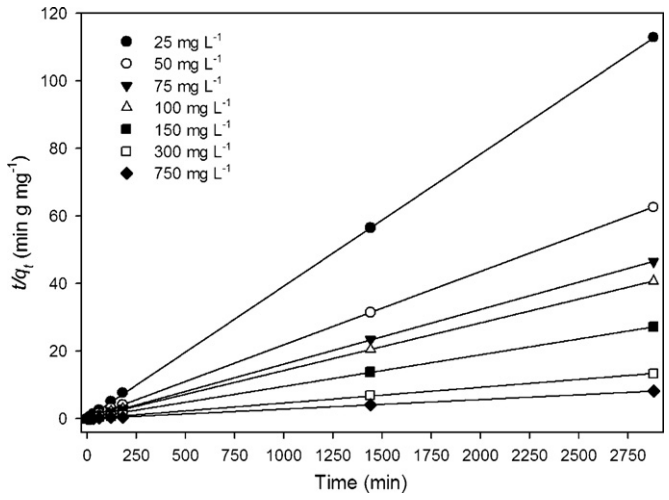

Fig. 5. Pseudo second-order kinetic plot for the adsorption of RR 120 on *Spirogyra majuscula*.

These results were also observed in the adsorption of reactive dyes on *C. vulgaris* [20], the removal of basic dye on *Caulerpa lentillifera* [15], the adsorption of indigo carmine on rice husk ash [26] and the adsorption of basic yellow dye on *C. scalpelliformis* [10].

3.4. Equilibrium modeling

Equilibrium adsorption studies are related to the capacity of adsorbent. Langmuir, Freundlich and Redlich-Peterson models are used to describe the non-linear equilibrium adsorption between adsorbed material on the cells (q_{eq}) and unabsorbed pollutant in solution (C_{eq}) [3,15].

The Langmuir model [27] assumes that solid surface has a finite number of identical sites which shows homogeneous surfaces. The linearized form of Langmuir equation is given as Eq. (7):

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_o b} + \frac{C_{eq}}{q_o} \quad (7)$$

where C_{eq} is the equilibrium concentration of RR 120 (mg L^{-1}) in the solution, q_{eq} (mg g^{-1}) is the amount of adsorbed dye per unit weight of the algal adsorbent at equilibrium, q_o is the maximum monolayer adsorption capacity (mg g^{-1}) and b is the Langmuir constants (L g^{-1}).

The Langmuir model can also expressed by means of a dimensionless constant, R_L, whose magnitude provides information about whether the adsorption process is spontaneous or non-spontaneous. It can be calculated by using Eq. (8).

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where C_0 is the initial dye concentration and b is the Langmuir constant. The value of R_L indicates adsorption process is irreversible when R_L is 0; favorable when R_L is between 0 and 1; linear when R_L is 1; and unfavorable when R_L is greater than 1 [28].

The experimental data was fitted to Freundlich model to describe the dye uptake on the algal adsorbent [29]. The Freundlich equation is given by Eq. (9):

$$q_{eq} = K_F C_{eq}^{1/n} \quad (9)$$

where K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively [29].

Redlich-Peterson equation has been used to improve the fitting by Langmuir or Freundlich equation [30]. Redlich-Peterson equation is given by Eq. (10):

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \quad (10)$$

where $K_{R\text{-}P}$, $a_{R\text{-}P}$ and β are the Redlich-Peterson parameters. The values of β lie between 0 and 1, which indicates the adsorption is favored. This equation reduces to Henry's equation when β is 0 and converts to the Langmuir equation when β is 1 [30].

Parameters and correlation coefficients obtained from Langmuir, Freundlich and Redlich-Peterson models are summarized in Table 3. They had high correlation coefficients ($R^2 > 0.90$), which indicated that these models could be regarded as sufficient to

Table 4
Explanations of different error functions.

Error function	Abbreviation	Formula	References
Marquardt's percent standard deviation	*MPSD*	$MPSD = 100\sqrt{\frac{1}{m-p}\sum_{i=1}^{m}\left(\frac{q_{exp}-q_{cal}}{q_{exp}}\right)_i^2}$	[29]
The average relative error	*ARE*	$ARE = \frac{100}{m}\sum_{i=1}^{m}\left\lvert\frac{q_{exp}-q_{cal}}{q_{exp}}\right\rvert_i$	[30]
The average relative standard error	*ARS*	$ARS = \sqrt{\frac{\sum_{i=1}^{m}[(q_{cal}-q_{exp})/q_{exp}]^2}{m-1}}$	[19]

describe adsorption of RR 120 on *S. majuscula* (Table 3). The highest q_o value was found as 772.44 mg g^{-1} from Langmuir model. Previously, the highest q_o of RR 120 uptake on *Lentinus sajor-caju* [7] and remazol black B on *C. vulgaris* [20] were found to be 182.9 and 515.6 mg g^{-1}, respectively. These results indicated that *S. majuscula* showed a great performance for the removal of RR 120 dye from aqueous solution. The R_L values ranged between 0.15 and 0.36. The R_L values confirmed that the adsorption process is favorable (Table 3). Similar results were also found in previous studies [17,28].

The Freundlich model constants, K_F and n give information about the adsorption capacity and adsorption intensity, respectively. The magnitudes of K_F (4.30–8.84) and n (1.43–2.38) showed easy separation of RR 120 from aqueous solution. It can regarded that *S. majuscula* had high capacity for the adsorption of RR 120, in agreement with results of previous studies [17,21,24]. The suitability of Freundlich model shows that the adsorption process could be a heterogeneous surface with a non-uniform distribution of adsorption.

The Redlich-Peterson model parameter, $K_{R\text{-}P}$, (49.87–74.16) indicated that *S. majuscula* had higher capacity for the adsorption, in agreement with Aksu and Karabayır [5]. The constant of Redlich-Peterson, β, varied from 0.31 to 0.59, which indicated the adsorption of RR 120 was favored on the algal adsorbent. Therefore, this model could be reported as sufficient to describe the adsorption of RR 120 on *S. majuscula*. Lakshmi et al. [26] stated that the adsorption is more heterogeneous in nature, when β equals to $[1-(1/n)]$. The values of β were nearly equal to $[1-(1/n)]$ (Table 3). Therefore, it could be stated that the adsorption of RR 120 on *S. majuscula* was more heterogeneous in nature, in agreement with finding of Lakshmi et al. [26].

The plots of q_{eq} against C_{eq} (Fig. 6) at various initial RR 120 concentrations indicated the applicability of Langmuir, Freundlich and Redlich-Peterson models. Adequacy of these models

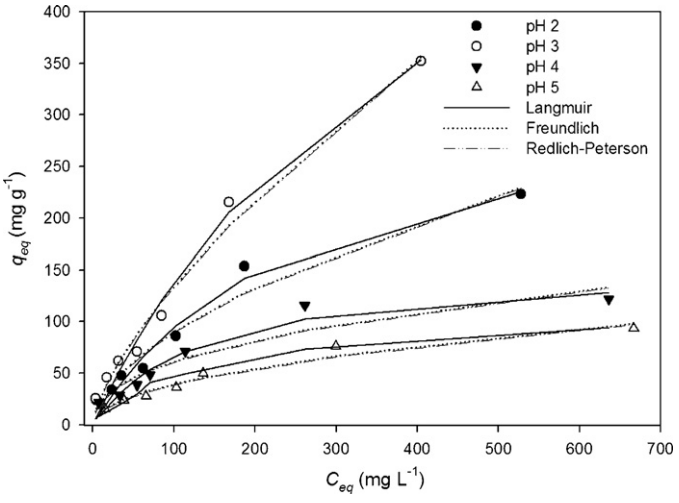

Fig. 6. Comparison of experimental and predicted data from Langmuir, Freundlich and Redlich-Peterson models.

Table 5
Values of different error analyses of equilibrium models for the adsorption of reactive red 120 on *Spirogyra majuscula*.

Model	pH	*MPSD*	*ARE*	*ARS*
Langmuir	2	36.63281	20.95616	0.33441
	3	41.16113	24.61713	0.37575
	4	29.34697	15.62934	0.26790
	5	22.6253	12.65366	0.20654
Freundlich	2	22.09761	15.42699	0.201723
	3	27.07799	16.92707	0.247187
	4	21.47984	15.27202	0.196083
	5	11.71939	9.083367	0.106983
Redlich-Peterson	2	25.60419	15.02608	0.209057
	3	32.34317	17.90461	0.264081
	4	22.68366	15.22798	0.185211
	5	11.6114	7.773209	0.094807

Abbreviations are given in Table 4, i.e., *ARE* is the average relative error.

for the adsorption of RR 120 on *S. majuscula* implied that both monolayer adsorption and heterogeneous surface conditions were present under the studied conditions (Table 3; Fig. 6). The parameters of equilibrium models indicated easy uptake of RR 120 from aqueous solution with high adsorptive capacity of *S. majuscula*. Mentioned three adsorption models also showed better fit for the adsorption of reactive black 5 on *Laminaria* sp. [3], the removal of gryfalan black RL dye on different kinds of fungi [5] and the adsorption of methylene blue on *Scirpus tabernaemontani* [17].

Three different error functions were applied to find out the most appropriate equilibrium model to describe the adsorption of RR 120 [16,21,24]. The Marquardt's percent standard deviation (*MPSD*) [31], the average relative error (*ARE*) [32] and the average relative standard error (*ARS*) [21] were used in the present study. Equations of these error functions and their results are given in Tables 4 and 5, respectively. Despite Langmuir, Freundlich and Redlich-Peterson models had similar high correlation coefficients (Table 3), results of the error functions (Table 5) indicated that Freundlich and Redlich-Peterson models were more appropriate to describe the adsorption of RR 120, which is usually adopted for heterogeneous adsorption in agreement with findings of Özer et al. [9].

4. Conclusions

The present study revealed *S. majuscula* had a potential to remove RR 120 from aqueous solution at different pH regimes. The behavior of batch adsorption kinetics was well described by pseudo second-order kinetic model. From the results of R^2 and the error functions, Freundlich and Redlich-Peterson models were well fitted to the experimental data than those of Langmuir model. Consequently, this green alga undoubtedly had a potential for the removal of RR 120 rapidly and efficiently without excessive cost.

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