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Adsorption of acid orange II dye by raw and chemically modified brown macroalga *Stoechospermum marginatum*

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ABSTRACT

The adsorption of acid orange II (AO7) dye from aqueous solution was examined onto untreated and chemically modified forms (treated with (i) propylamine, (ii) acidic methanol, (iii) formaldehyde and (iv) formic acid with formaldehyde) of brown alga, *Stoechospermum marginatum*. The adsorption was studied as a function of initial solution pH (2.0–10.0), initial dye concentration (30–90 mg/L), contact time (5–60 min) and biomass dosage (0.2–2.2 g/L) at constant temperature and agitation speed. The kinetic data were well described with the pseudo-second-order model. The results revealed that amine functional groups were mainly responsible for the adsorption of acid orange II dye. The modification of biomass with propylamination enhanced the dye adsorption capacity about two times of the untreated algal biomass. These findings were confirmed by Fourier transform infrared (FT-IR) spectroscopy.

1. Introduction

The increasing use of dyes in various industrial applications has resulted in the discharge of toxic dye effluents into the water streams causing serious environmental pollution. Dyes are mainly used in textiles, plastics, tanneries, pharmaceuticals, leather, packed food, pulp and paper, paint and electroplating industries [1,2]. Dyes are considered as obnoxious type of pollutants as they impart color to water which is not acceptable due to esthetic consideration. Dyestuff wastes are known to be toxic [3], carcinogenic [4], mutagenic [5], and teratogenic [6]. Dyes are generally resistant to light, water, oxidizing agents and many chemicals and therefore difficult to degrade once released into the aquatic systems [7,8]. Hence, the removal of dyes from water and wastewaters is important before they are mixed up with unpolluted natural water resources.

Conventional methods such as, anaerobic treatment, trickling filters, flotation, chemical coagulation, electrochemical coagulation, membrane separation, advanced oxidation processes, adsorption and photo-degradation have been applied for dye removal from water and wastewaters [9–13]. However, major disadvantages of these methods include production of toxic sludge, high operational cost, technical limitations, usually dependent on the concentration of the waste, lack of effective color reduction and sensitivity to a variable wastewater input as reported by many researchers. Adsorption using activated carbon is undoubtedly one of the most suitable techniques for treating water and wastewater containing toxic pollutants including dyes, however, it is sometimes not economical due to the expensive cost of commercial activated carbon. Therefore, research is directed toward the development of low-cost adsorbents alternative to activated carbon. In the past years, many low cost materials have been tested for dye adsorption [14–19]. However, the developed adsorbents have shown low adsorption potential for dye removal, therefore, a large amount of adsorbents would be needed to treat dyes containing industrial effluents.

In recent years, biosorption process has gained wide attention for treating metal or dye bearing effluents. An inexpensive source of biomass is present, in copious quantities, in the oceans as seaweeds, represented by several marine algae. Marine algae have been found to possess high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the cell wall surface containing various functional groups such as amino, hydroxyl, carboxyl and sulfate, which can act as binding sites for metals. Modification of the biomass is often carried out to improve the biosorbent's properties or physical performance. Physical pre-treatment methods such as heating, autoclaving, and chemical pre-treatments such as acids, alkalis and organic chemicals showed enhancement or reduction in metal biosorption, depending on the biomass type and treatment procedures used [20–23].

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Acid orange 7 (AO7) is an azo dye and is widely used in a variety of industries ranging from textile to paper [24]. Its toxicity is between those highly toxic compounds (phenolic and metals) and other organic compounds like formalin [25]. Active azo dyes contain an azo group (–N=N–), as a part of their structure [26], so, they could cause harmful health effects and it is therefore, essential to properly treat industrial wastewaters containing this dye. Many studies have been conducted for the removal of AO7 dye from aqueous solution using microorganisms [27], biodegradation [13], algae [28,29], oxidative radiolysis [30–33], and the photo-Fenton process [34–36]. However, there is less information on the use of brown macroalga as biosorbent for the removal of acidic dyes. In this work, the potential of marine alga (*Stoechospermum marginatum*) to remove acid orange 7 dye is studied. The role of different functional groups, namely carboxyl, amine and/or amide and hydroxyl, present on the algal biomass, was examined for the biosorption of the dye.

2. Experimental

2.1. Chemical reagents and adsorbate

AO7 dye was purchased from Alvan Sabet, Iran. The structure of AO7 dye along with its important characteristics are listed in Table 1. Dye stock solution of 1000 mg/L was prepared by dissolving weighed amount of AO7 dye in 1 L of distilled water and the solutions for all experiments were prepared through dilutions of stock solution. The desired solution pH was adjusted with diluted NaOH and HCl. All the reagents used were of analytical grade.

2.2. Biomass

The brown macroalga, *S. marginatum*, was used as biosorbent for the biosorption of AO7 dye. Samples of marine alga were collected from the Oman Sea coast of Chabahar, Iran in March, 2010. The alga biomass was first washed with tap water, then several times with distilled water to remove the extraneous materials and salts. The biomass was sun-dried for three days and then dried in an oven at 70 °C for 24 h. The dried alga biomass was cut, sieved and the particles in the range of 106–250 μm were used for the experiments.

2.3. Pretreatment of biomass

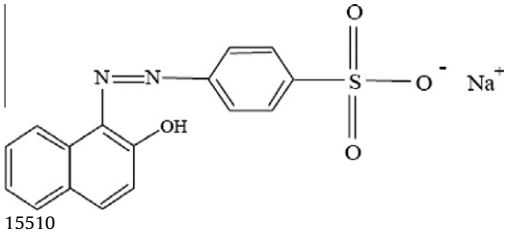
2.3.1. Esterification

Five grams of biomass was added to anhydrous methanol (500 mL) and conc. HCl (4.15 mL) in 1000 mL conical flask. The reaction mixture was agitated on a rotary shaker (Labcon, FSIM-SPO16, United States) for 3 h with a shaking speed of 145 rpm at 50 °C, and then kept without shaking for 24 h. This treatment results in the esterification of the carboxylic groups of biomass [37]. The general reaction scheme is

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O \quad (1)$$

Afterward, the biomass was washed several times with deionized water and dried at 70 °C for 24 h.

Table 1
General characteristics of acid orange 7 dye.

Chemical structure	
C.I. number	15510
C.I. name	Acid orange II
Chromophore	Monoazo
Ionization	Acidic
Molecular weight (g/mol)	350.32
λmax (nm)	485

2.3.2. Formaldehyde treatment

Two-hundred milliliters of pure formaldehyde was added to 10 g of smoothly crushed biomass and the reaction mixture was shaken on a rotary shaker for 3 h with agitation speed of 145 rpm at 50 °C. After reaction, biomass was dried at 70 °C for 24 h.

2.3.3. Methylation of amines

The modification of amino functional groups was done by shaking 10 g (dry weight) of the dried biomass in a conical flask containing 200 mL of pure formaldehyde (HCHO) and 400 mL of formic acid (HCOOH) for 3 h with agitation speed of 145 rpm at 50 °C [38]. This treatment resulted in methylation of amine. The general scheme for this reaction is:

$$RCH_2NH_2 \xrightarrow{HCHO,\ HCOOH} RCH_2N\ (CH_3)_2 + CO_2 + H_2O \quad (2)$$

2.3.4. Propylamination of amides

Five-hundred milliliters of 0.1 M propylamine was added to 10 g (dry weight) of dried biomass. The reaction mixture was shaken on a rotary shaker for 3 h with agitation speed of 145 rpm at 50 °C; subsequently biomass was dried at 70 °C for 24 h. This reaction lead to the conversion of carboxylic acid groups to amide group [39] by the following reaction:

$$R\text{-}COOH + CH_3CH_2CH_2NH_2 \rightarrow R\text{-}COONH_2 + C_3H_6 \quad (3)$$

2.4. Batch experiments

The batch experiments were conducted in 100 mL Erlenmeyer flasks containing 50 mL of dye solution. A weighed amount of sorbent was added to dye solutions. The mixtures were shaken on a rotary shaker (Labcon, FSIM-SPO16, United States) at 130 rpm for 1 h at 25 °C. The effect of pH (2.0–10.0), initial dye concentration (30–90 mg/L), sorbent dose (0.2–2.2 g/L), and contact time (5–60 min) was evaluated in order to find the optimum conditions for the dye biosorption. Control experiments were also performed without the addition of biosorbent to confirm that the adsorption of the dye onto conical flasks was negligible. All adsorption experiments were performed in triplicate, and the mean values were used in data analysis.

After equilibrium, the solution was filtered and the filtrates were subsequently analyzed for residual dye concentration with UV/vis Spectrophotometer (Hach, DR/4000 Spectrophotometer, United States) at the maximum absorption wavelength (485 nm).The percent dye removal by alga biomass was computed using the following equation (Eq. (4)):

$$\text{AO7 removal efficiency}(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (4)$$

where, C_i and C_e are the initial and equilibrium concentrations of AO7 dye (mg/L). The amount of dye adsorbed q_e was calculated using the mass balance equation given by Eq. (5): -

$$q_e = \frac{V(C_i - C_e)}{m} \quad (5)$$

where q_e is the dye uptake (mg/g), V is the solution volume (L) and m is the mass of biosorbent (g).

2.5. Adsorption kinetics

Adsorption kinetic experiments were conducted in 500 mL conical flasks containing 250 mL of the dye (50 mg/L) and biosorbent dose of 1 g/L biosorbents. The flasks were agitated on a rotary shaker at 130 rpm under constant temperature (25 ± 2 °C). The samples were taken at predetermined time intervals, filtered and analyzed for the residual dye concentrations. The kinetic data were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

2.6. Adsorption isotherms

Adsorption isotherm experiments were conducted by equilibrating *S. marginatum* biomass (untreated and treated, 1 g/L) in 100 mL Erlenmeyer flasks containing 50 mL of dye solutions of varying initial dye concentrations (10–50 mg/L). The mixture was shaken on a rotary shaker (Labcon, FSIM-SPO16, United States) at 130 rpm by keeping the temperature constant (25 ± 2 °C). After equilibrium, samples were filtered and analyzed for the residual dye concentrations. Adsorption equilibrium data were analyzed using adsorption isotherm models viz., Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin models.

2.7. FT-IR analysis

FT-IR spectra were recorded with a Jasco-680 (Japan) spectrometer in the range of 400–4000 cm^{-1}. Biosorption experiments were performed with a 100 mL dye solution with an initial concentration of 50 mg/L, initial pH 2.0 and biosorbent dose of 1.0 g/L. Samples were equilibrated from 0 min (control) to 24 h. The pure (without dye biosorption experiment) and dye-loaded (after biosorption experiment) biomass were dried at 50 °C for 24 h. The samples were mixed with KBr and then ground in an agate mortar at an approximate ratio for the preparation of pellets. The background obtained from KBr disc was automatically subtracted from the sample discs spectra.

3. Results and discussion

3.1. Effect of initial solution pH

The initial solution pH significantly influences the overall adsorption process [14]. The pH affects both the solubility of the dye and ionization states of functional groups, such as amine, carboxyl and hydroxyl onto pectin- and cellulose-rich sorbents [40]. The effect of initial solution pH on the adsorption of AO7 dye onto untreated and treated biosorbents was studied by varying the pH from 2 to 10, while the initial dye concentration, temperature, biosorbents dosage and contact time were kept constant at 50 mg/L, 25 ± 2 °C, 1 g/L and 60 min, respectively. The plot of dye uptake versus pH is shown in Fig. 1. As can be seen from this figure, little adsorption took place at the initial pH range of 4.0–10.0. Adsorption capacity of AO7 dye increased with decreasing the initial solution pH from 4.0 to 2.0 and maximum adsorption was obtained at pH 2.0 for all chemically modified and untreated brown alga. Higher uptakes obtained at lower pH might be due to the electrostatic interaction between negatively charged dye ions and positively charged cell surface [41,42]. The variation in the uptake capacity of *S. marginatum* biomass across the pH range may be explained in terms of its effective isoelectric points. Isoelectric point of ca. pH 3.0–4.0 has been reported for most algal species [43,44].

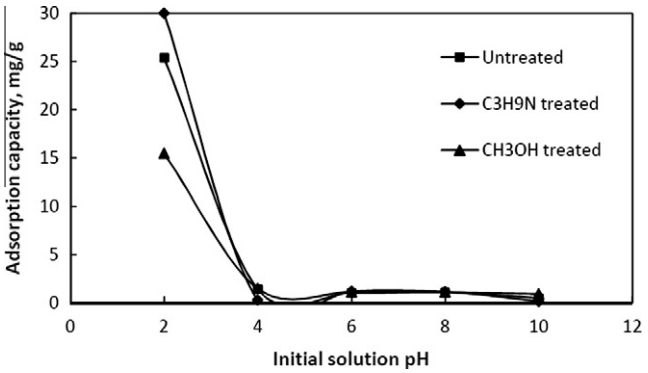


Fig. 1. Effect of initial solution pH on the removal of AO7 dye by untreated and modified *S. marginatum* biomass (T = 25 ± 2 °C, $[AO7]_o$ = 50 mg/L, algae dose = 1 g/L).

Biomass surface possesses positive charge when solution pH is less than isoelectric point, and observes a reverse trend when isoelectric point pH is more than solution pH. Since AO7 dye is an anionic dye, which is negatively charged, the acidic solution would favor the dye adsorption onto biomass surface, thus the dye adsorption increases. The decrease in biosorption of the dye with increasing initial pH could be attributed to the change in surface characteristics and charge. At high pH, a high concentration of OH^- could neutralize the positively charged surface of biomass and forms a negatively charged surface. Thus, it would increase repulsion between colored dye ions and the negatively charged biomass and cause a decrease in the biosorption capacity. As maximum adsorption of AO7 dye for all biosorbents was observed at pH 2.0, therefore, further sorption studies were carried out at solution pH 2.0. Similar results have also been reported in the literature where the low pH was found to be favorable for anionic dyes sorption [45].

3.2. Effect of contact time

In order to determine the optimum contact time for AO7 dye adsorption, untreated and treated biomass, *S. marginatum* (1 g/L) was equilibrated with 250 mL of AO7 dye solution with an initial concentration of 50 mg/L at pH 2.0. It was noticed that maximum biosorption of the dye occurred within the first 20 min of contact time; thereafter, the adsorption decreased gradually and equilibrium was attained in about 60 min (Fig. 2). The higher uptake of the dye during the initial stage of biosorption might be due to the availability of a larger number of vacant surface sites for dye biosorption. After occupying most of the available site, the remaining vacant surface sites were difficult to be occupied due

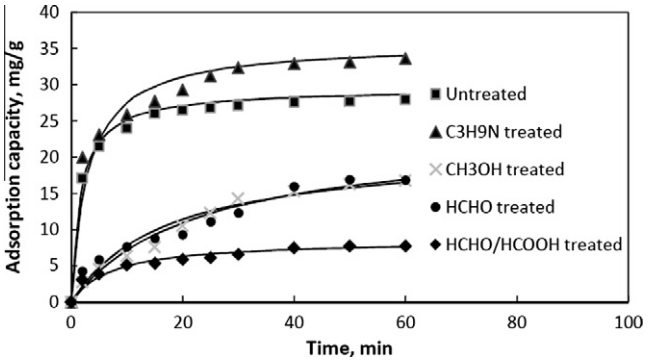


Fig. 2. Effect of contact time on the removal of AO7 dye by untreated and modified *S. marginatum* biomass (pH = 2, T = 25 ± 2 °C, $[AO7]_o$ = 50 mg/L, algae dose = 1 g/L).

to the repulsive forces between dye adsorbed on the algal biomass and solution phase [46]. Similar results have also been reported in the literature where rapid uptake of the dye on many biosorbents has been observed during the initial stages of the contact time, followed by the slower adsorption near the equilibrium [47].

3.3. Effect of initial dye concentration

Fig. 3 depicts the effect of different initial concentrations of AO7 dye (30–90 mg/L) on the adsorption of all the chemically modified and untreated brown alga, *S. marginatum*. It can be seen that the adsorption of the dye at different concentrations is rapid in the initial stages and gradually decreases with the progress of adsorption until the equilibrium is reached. The initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence a higher initial concentration of the dye will enhance the adsorption process. Additionally, it is suggested that increasing the initial concentration of the dye increases the probability of contact between dye molecules and algal biomass [48].

The dye adsorption increased from 20.50 to 31.89 mg/g onto untreated biomass and 20.30 to 45.47 mg/g for propylaminated-treated biomass by increasing the initial dye concentration from 30 to 90 mg/L. The adsorption capacity of propylamine-treated biomass increased significantly as compared to the untreated and other pretreated biomasses with the increase of the initial dye concentration. The reason for a higher dye uptake on propylamine-treated biomass could be due to the presence of amine functional groups in the treated biomass which were presumably responsible for the adsorption of AO7 dye from aqueous solution. The results suggested that treatment of biomass with propylamine increased amine functional group density on the biomass surface and this facilitates electrostatic interaction between biopolymer and the negatively charged anionic dye, especially at higher dye concentrations.

3.4. Kinetic modeling

The adsorption kinetics is an important parameter for designing adsorption systems and is required for selecting the optimum operating conditions for pilot-scale process. The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied to understand the sorption kinetics. The linear form of the pseudo-first-order equation is given as [49]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}.t \tag{6}$$

where, q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo-first-order kinetics. In the case of pseudo-first-order model, the R^2 values were found to be low, as shown in Table 2. Furthermore, there were significant differences between the calculated and experimental uptake values, suggesting that the sorption kinetics does not follow pseudo-first-order kinetics.

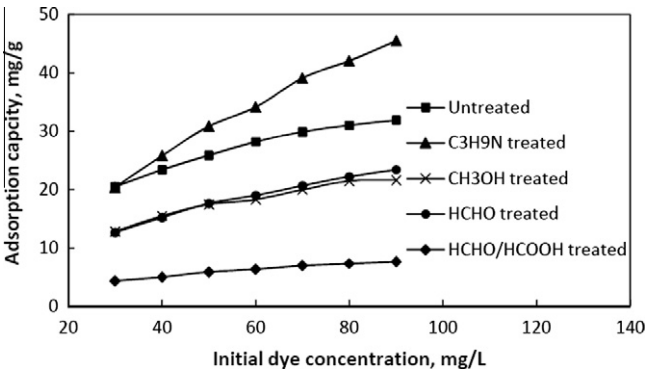


Fig. 3. Effect of initial dye concentration on the removal of AO7 dye by untreated and modified *S. marginatum* biomass (pH = 2, T = 25 ± 2 °C, algae dose = 1 g/L).

The experimental data were examined by the pseudo-second-order kinetic model which is given by the following equation [50]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{7}$$

where, q_e and q_t have the same meaning as mentioned previously, and k_2 is the rate constant for the pseudo-second-order kinetics. The rate constant, and the R^2 values are compiled in Table 2. It was found that the calculated uptake values are close to the experimental values in case of pseudo-second-order kinetic model. It can be explained that first, the initial rapid phase may involve physical adsorption or ion exchange at cell surface and the subsequent slower phase may include other mechanisms such as complexation, micro-precipitation or saturation of binding sites. It is important to note here that differences in adsorption dynamics and values between different biomass could be due to the differences in structural properties such as, protein and aminated composition and surface charge density, topography and surface area, which may influence adsorption rate [51].

The kinetic data were also applied to the intraparticle diffusion model which is expressed as [52]:

$$q = k_{id}t^{0.5} + C \tag{8}$$

where, q (mg/g) is the amount of AO7 dye adsorbed at time t, C is the intercept, and k_{id} is the intraparticle diffusion rate constant. Different phases were observed in the resulting plots (Fig. 4), representing different stages in adsorption: an initial phase followed by linear portion and then a plateau. The initial phase might be due to the surface adsorption and rapid external diffusion (boundary layer diffusion). The second linear portion is the gradual adsorption stage where the intraparticle diffusion is rate controlled. The plateau (third portion) is the final equilibrium stage, where the intraparticle diffusion starts to slow down due to the low solute concentration in solution as shown in Fig. 4 [40]. It has been reported by various researchers that when the plots do not pass through the origin, this is indicative of some degree of boundary layer control and further shows that the intraparticle diffusion is not only the rate controlling step, but some other processes may also control the rate of adsorption. These results suggest that the adsorption of the dye probably takes place through surface exchange reactions until the surface functional sites are fully occupied; thereafter dye molecules diffuse into the porous biomass for further interaction.

3.5. Adsorption isotherms

Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) models were examined for adsorption isotherm modeling of experimental data. Based on the assumption, Langmuir model can be expressed as follows [53]:

$$q_e = \frac{q_{\max} b C_e}{1 + bC_e} \tag{9}$$

where q_e (mg/g) and C_e (mg/L) are the amounts of dye adsorbed per unit weight of biomass and dye equilibrium concentration in solution at equilibrium, respectively. The $q_{\max}$ (mg/g) indicates the monolayer sorption capacity of adsorbent and the Langmuir constant b is related to the energy of adsorption. The Langmuir isotherm model did not exhibit good fit to the experimental

Table 2
Kinetic parameters obtained for pseudo-first-order, pseudo-second-order and intraparticle diffusion model for AO7 dye biosorption by untreated and treated *S. marginatum* biomass, pH = 2, T = 25 ± 2 °C, $[AO7]_o$ = 50 mg/L, algae weight = 1 g/L.

Biomass	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	$k_{1\times10^2}$ (1/min)	q_1 (mg/g)	R^2	$k_{2\times10^2}$ (g/mg min)	q_2(mg/g)	R^2	$k_{id\times10^1}$ (mg g $min^{-0.5}$)	C (mg/g)	R^2
Untreated *S. marginatum*	6.00	7.97	0.93	2.03	29.41	0.99	1.49	18.24	0.78
C_3H_9N treated *S. marginatum*	5.10	6.91	0.75	0.93	35.71	0.99	2.18	18.69	0.92
CH_3OH treated *S. marginatum*	0.68	20.31	0.97	0.19	23.26	0.95	2.43	−0.07	0.97
HCHO treated *S. marginatum*	5.50	19.26	0.91	0.27	21.28	0.92	2.18	0.69	0.97
HCHO/HCOOH treated *S. marginatum*	4.60	4.54	0.70	1.63	8.55	0.99	0.76	2.31	0.97

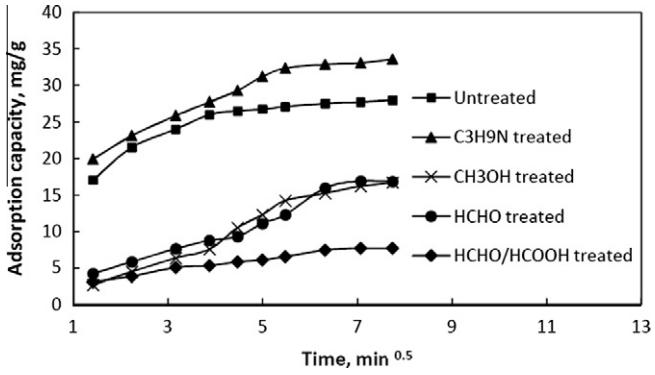


Fig. 4. Intraparticle diffusion model plots for the biosorption of AO7 dye by untreated and modified *S. marginatum* biomass (pH = 2, T = 25 ± 2 °C, $[AO7]_o$ = 50 mg/L, algae dose = 1 g/L).

equilibrium data as low correlation coefficient (R^2) values were observed for all biomass (Table 3).

Freundlich isotherm can be expressed as follows [54]:

$$q_e = K_f C_e^{1/n} \tag{10}$$

where q_e is solid phase sorbate concentration in equilibrium (mg/g), C_e is liquid phase sorbate concentration in equilibrium (mg/L), K_f is Freundlich constant (mg/g) and $1/n$ is an empirical parameter relating the sorption intensity, which varies with the heterogeneity of the material. All the $1/n$ values obtained from the Freundlich model are less than unity for all the biomasses indicating that adsorption of AO7 dye on the biomass is favorable. Furthermore, the high values of R^2 for all biomass indicated that the Freundlich model could be used favorably to describe the experimental data for the adsorption of AO7 dye on untreated and pretreated *S. marginatum* biomass (Figs. 5(a–e)).

The nature of adsorption (physical or chemical) was also analyzed by D–R isotherm. The D–R isotherm model can be expressed as [55]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{11}$$

where, q_e is the amount of dye adsorbed per unit mass of adsorbent, q_m is the theoretical adsorption capacity, β is the constant of the sorption energy, which is related to the average energy of sorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution, and ε is Polanyi potential, which is described as:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{12}$$

where T is the temperature (K) and R is the gas constant. The value of mean sorption energy, E, can be calculated from D–R parameter β as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{13}$$

The E (kJ/mol) value gives information about adsorption mechanism. If it lies between 8 and 16 kJ/mol, the adsorption process is controlled by a chemical mechanism, while for E <8 kJ/mol, the adsorption process proceeds through a physical mechanism [56]. The values obtained (Table 3) suggested that biosorption of the dye occurs via physical mechanism.

Temkin isotherm was also applied to evaluate the experimental data. Unlike the Langmuir and Freundlich models, the Temkin isotherm model takes into account the interactions between adsorbent and dye to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [50]:

$$q_e = \frac{RT}{b_T}\ln(A_T C_e) \tag{14}$$

where, A_T (L/mg) and, b_T, are isotherm constants, T is the temperature (K), and R is the ideal gas constant (8.314 J/mol K). The Temkin constants were calculated and are listed in Table 3. The determination coefficients values for all the biomass were found to be high indicating the applicability of Temkin model. The results implied that the surface of biosorbents did not possess equal distribution of binding energies on the available binding sites [57].

3.6. Effect of adsorbent dose

Biosorbent dosage is an important parameter as it determines the percentage of decolorization and may also be used to predict the cost of biomass per unit of the dye solution to be treated. The effect of varying the biomass dosage (0.2–2.2 g/L) on AO7 dye adsorption was examined using 50 mL dye solution (50 mg/L) under optimized conditions of pH and contact time and the

Table 3
Isotherm constants of AO7 dye biosorption by untreated and treated *S. marginatum* biomass, pH = 2, T = 25 ± 2 °C, $[AO7]_o$ = 50 mg/L, algae weight = 1 g/L.

Biomass	Langmuir model			Freundlich model			D–R model				Temkin model		
	q_m (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2	q_s (mg/g)	$k_{ad\times10^5}$ (mol^2/kJ^2)	E (kJ/mol)	R^2	b_T	A_T (L/mg)	R^2
Untreated *S. marginatum*	35.62	0.14	0.92	11.76	3.92	0.99	0.60	29.78	0.29	0.81	374.99	2.40	0.99
C_3H_9N treated *S. marginatum*	71.05	0.04	0.95	6.33	1.85	0.99	1.00	29.08	0.22	0.88	145.91	0.36	0.99
CH_3OH treated *S. marginatum*	29.08	0.05	0.97	4.39	2.54	0.99	2.00	21.31	0.16	0.93	368.36	0.42	0.99
HCHO treated *S. marginatum*	34.06	0.04	0.98	3.43	2.13	0.99	3.00	22.47	0.13	0.91	300.20	0.27	0.99
HCHO/HCOOH treated *S. marginatum*	14.95	0.02	0.97	0.82	1.92	0.99	7.00	7.65	0.08	0.92	813.65	0.16	0.99

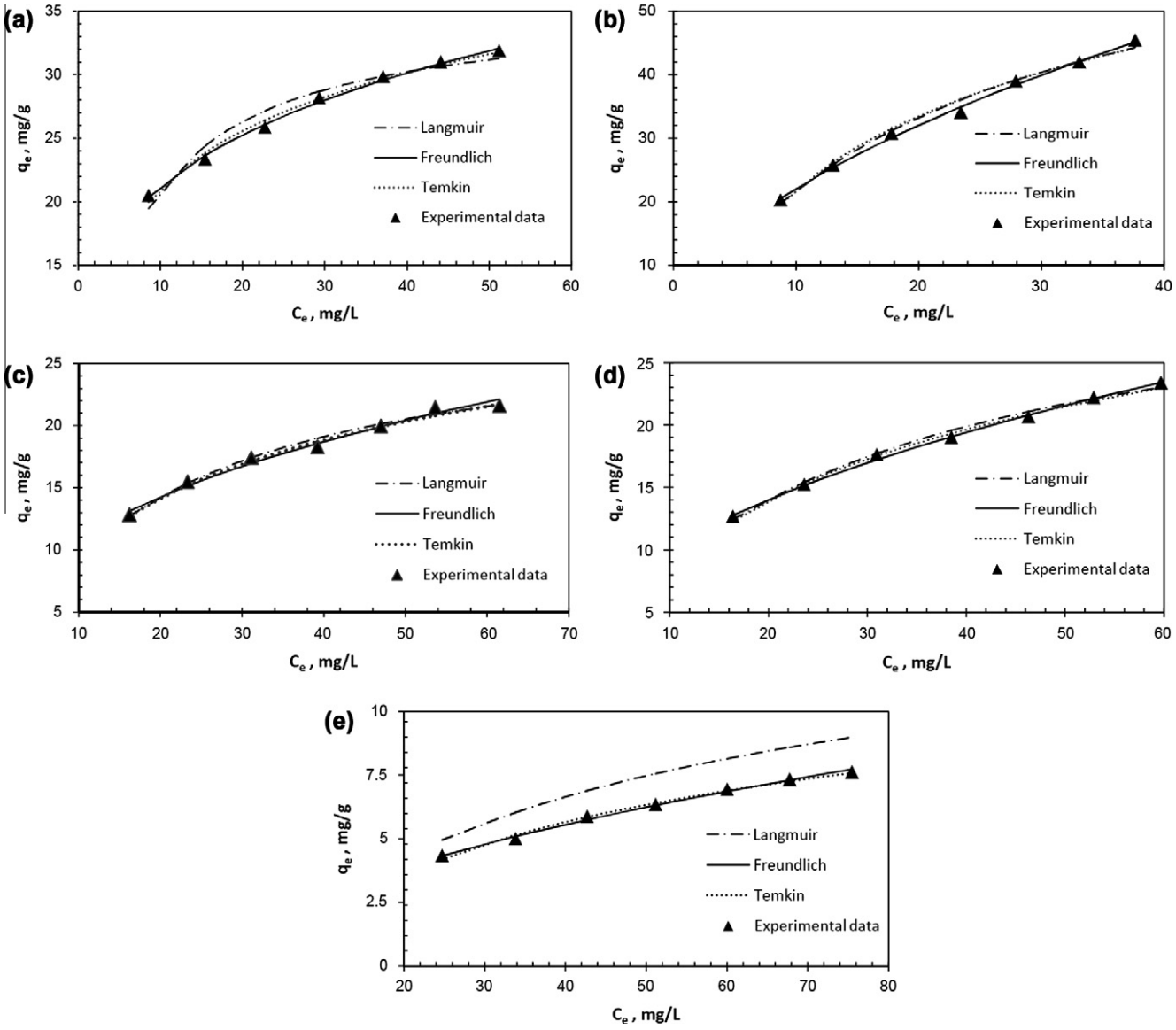


Fig. 5. Adsorption isotherms of AO7 dye by (a) untreated, (b) C_3H_9N treated, (c) CH_3OH treated, (d) HCHO treated, (e) HCHO/HCOOH modified *S. marginatum* biomass (pH = 2, T = 25 ± 2 °C, algae dose = 1 g/L).

results are presented in Fig. 6. As can be seen from the figure, increasing the biomass dosage increased dye uptake which could be attributed to increase in the surface area and availability of more dye binding sites by increasing the biomass dosage, thus enhancing the AO7 dye adsorption.

3.7. Effect of chemical modification of S. marginatum for AO7 dye sorption

The adsorption capacity of algae is attributed to their relatively high surface area and high binding affinity of ion exchanging sites [58]. Cell wall properties of algae play a major role in various processes including adsorption; electrostatic attraction, complexation and coagulation [59]. Extracellular polymers consist of surface functional groups, such as hydroxyl, carboxylate, amino and phosphate which are considered to be responsible for sequestration of dye and other contaminants from water and wastewater [60]. However, many researchers have reported unsatisfactory performance of native biomass due to their poor mechanical strength and low sorption capacity in low ion concentration [61,62]. The results of the present study showed that blocking of carboxyl, hydroxyl and amine groups by different chemical treatments significantly decreased the biosorption of AO7 dye, which implies that carboxyl, hydroxyl and especially amine groups play an important role in biosorption of AO7 dye. However, propylamine treatment of biomass increased the dye adsorption (Table 4).

During the esterification process, the numbers of carboxyl groups present on the cell surface decreased and consequently dye biosorption also decreased. Formaldehyde treatment of alga also resulted in the decrease of dye biosorption which can be explained by the masking effect of formaldehyde on the reactive sites [63]. The modification of algal cell wall with formaldehyde and formic acid greatly influenced the biosorption of the dye. Methylation of amine groups on the surface of alga significantly decreased dye adsorption. The methylation of amine groups prevents their participation in dye biosorption and hence reduces the biosorption efficiency. Therefore, the reduction in dye biosorption efficiency was observed when amine-methylated biosorbent was used revealing that the amine group present in the cell wall of alga contributes toward biosorption of the dye. Hence, the role of amine groups for

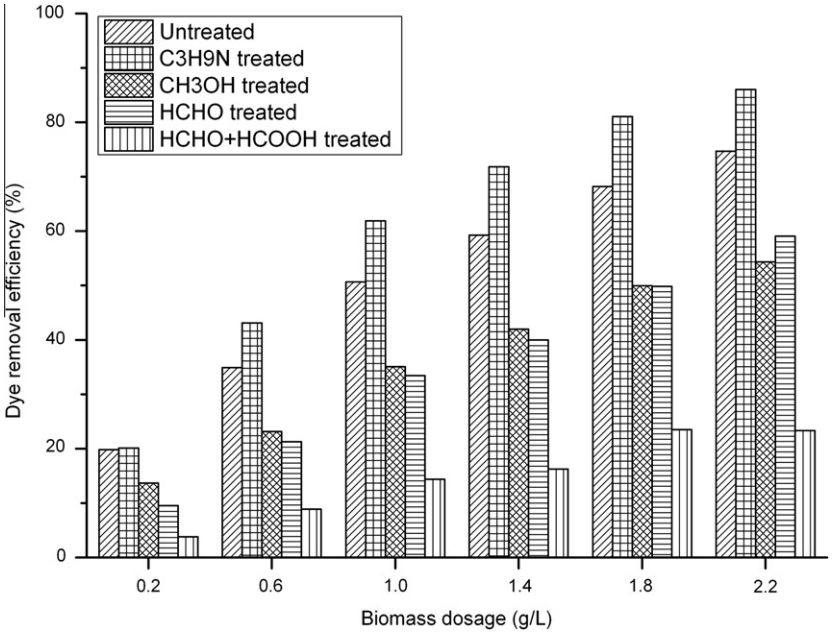


Fig. 6. Effect of algal biomass dosage on the removal of AO7 dye by untreated and modified *S. marginatum* biomass (pH = 2, $T = 25 \pm 2$ °C, $[AO7]_o = 50$ mg/L).

Table 4
Comparison of maximum uptake capacities of various sorbents reported in the literature for acid orange 7 dye sorption.

Sorbent	Initial concentration (mg/L)	pH	Sorbent dosage (g/L)	Temperature (°C)	Time (h)	q_m (mg/g)	Removal (%)	References
Powdered activated carbon	150	2.8	0.4	25	1.15		96.24	[30]
Soil	100	2	50	30	4	3.47	–	[46]
Ash	35	2	4	30		–	68	[51]
Soya	35		2	30		–	58	[51]
Oxihumolite	30–1400	1	20	22	72	50	–	[66]
Polymer	1000–3000	3	2	30	72	–	70	[66]
Guava seed carbon	50	2	30	15	24	–	100	[67]
Brewery grains	60	2	50	30	1	–	96	[68]
Waste Brewery's yeast	10	2	2	30	6	3.56	–	[69]
Azolla rongpong	0–800	2.5	4	30	12	76.92	–	[28]
Schizophyllum commune	100.1	2	20.4	30	12	44.23	–	[70]
Untreated *S. marginatum*	30–90	2	1	25	1	35.62	–	Present study
C_3H_9N treated *S. marginatum*	30–90	2	1	25	1	71.05	–	Present study
CH_3OH treated *S. marginatum*	30–90	2	1	25	1	29.08	–	Present study
HCHO treated *S. marginatum*	30–90	2	1	25	1	34.06	–	Present study
HCHO/HCOOH treated *S. marginatum*	30–90	2	1	25	1	14.95	–	Present study

adsorption of AO7 onto brown algal biomass is also important besides other functional groups. When the algal biomass was treated with propylamine, it gets adsorbed onto the negatively charged groups such as carboxyl, hydroxyl and phosphate groups on the algal biomass through their electrostatic interaction with positively charged amine groups of diluted propylamine solution. It might be possible that the dye adsorption increased significantly after a large number of amine groups were introduced on the surface of algal biomass. A comparison of maximum uptake capacities of various sorbents as reported in the literature for acid orange 7 dye is presented in Table 4. It is seen from this table that *S. marginatum* (untreated and treated forms) have comparable sorption potential for AO7 dye as compared to previously used sorbents. The differences in maximum sorption efficiencies of various sorbents might be due to different structures and sorption mechanisms of various sorbents and experimental conditions.

3.8. FT-IR analysis

The FT-IR experiment was conducted to obtain information on the possible interactions between the functional groups of biomass and AO7 ions. The FT-IR spectra of biomass before and after dye treatment are shown in Fig. 7. In the untreated *S. marginatum*, the broad and strong vibration around 3000–3600 cm^{-1} is indicative of the presence of the –OH groups and –NH groups on algal biomass. The peaks at 2923.56 cm^{-1} are due to the asymmetric and symmetric C–H stretching of the aliphatic groups. The strong peaks at 1630.52 cm^{-1} were attributed to stretching vibration of carboxyl group (–C = O). The peak at 1384.64 is due to –N = O stretching vibrations. The bands observed at 1035.59–1109.83 cm^{-1} were assigned to C–O stretching vibration of alcohols and carboxylic acids. Therefore, these bands confirm the lignin structure of the biomasses (Fig. 7a) [64,65]. Comparison of dye loaded biomass with FT-IR spectra of pure biomass displayed significant changes in some of the peaks. As can be seen in Fig. 7b, the shift and sharp reduction (3415.31 cm^{-1}) suggests the major role of –OH and –NH groups for AO7 adsorption onto algal biomass. The significant reduction in the peak at 1638.23 cm^{-1} reflects the effect of carboxyl group on the binding of AO7. The peak was shifted significantly and decreased in the band 1061.62–1032.69 cm^{-1} after dye sorption.

In the propylamine treated *S. marginatum*, there was a sharp shift and reduction at peak 3433.64 cm^{-1} (60.71%) to

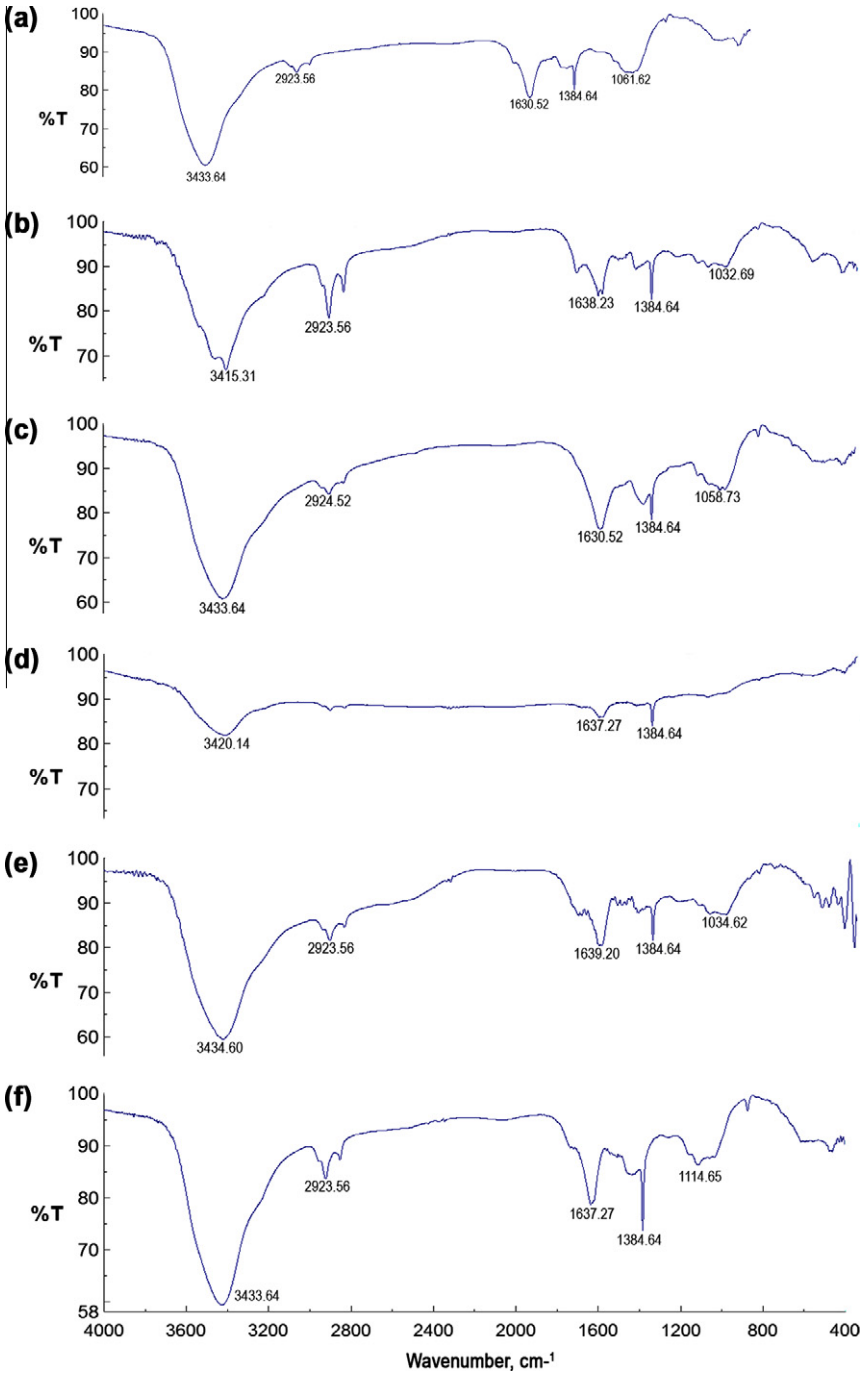


Fig. 7. FT–IR spectra of untreated and treated *S. marginatum* before and after dye biosorption (a) untreated alga before dye sorption, (b) untreated alga after dye sorption, (c) propylaminated alga before dye sorption, (d) propylaminated alga after dye sorption, (e) HCHO/HCOOH alga before dye sorption, and (f) HCHO/HCOOH alga after dye sorption.

3420.14 cm^{-1} (81.93%) that is indicative of the presence and high interaction of the –OH groups and –NH groups on algal biomass with AO7. This change in FT-IR spectra in the propylaminated *S. marginatum* is more significant than in the other tested algal biomasses. The peak at 2924.52 cm^{-1} is emitted. It can be attributed to the role of asymmetric and symmetric C–H stretching of the aliphatic groups in AO7 biosorption. The significant reduction in strong peaks from 1630.52 to 1637.27 cm^{-1} is indicative of the effect of carboxyl group in the biosorption process. The peaks were also significantly emitted in the bands of 1162.87–1034.62 cm^{-1} after dye sorption (Fig. 7c and d).

In the formaldehyde/formic acid treated *S. marginatum*, there was a slight shift and reduction at peak 3434.60 cm^{-1} (59.37%) to 3433.64 cm^{-1} (59.42%). This might be due to the blockage of $–NH_2$ functional group in treated algal biomass. The peaks at 2923.56 and 1384.64 cm^{-1} remained unchanged. The strong peaks at 1639.20 and 1034.62 cm^{-1} were shifted to 1637.27 and 1114.65 cm^{-1}. This indicated that the carboxyl group (–C=O) and C–O stretching vibration of carboxylic acids on treated algal biomass played a major role in AO7 dye biosorption (Figs. 7e and f). These observations indicate that several functional groups on the surface of the biomasses are responsible for binding of AO7 ions

in the adsorption process. Moreover, different adsorption capacities of AO7 onto these algal biomasses may be attributed to different interactions between dye molecule and the untreated and treated biomasses.

4. Conclusions

The present study revealed that the brown alga, *S. marginatum*, can be used as a suitable sorbent for the removal of acid dye, AO7 from dye solutions. The biosorption process depends significantly on the initial solution pH of the dye solution and is favored at pH 2.0. The results implied that the surfaces of biosorbents are heterogeneous in nature, physisorption process takes place through multilayer dye adsorption and did not possess equal distribution of binding energies on the available binding sites. According to the obtained results, the process followed pseudo-second-order kinetics. In the present study, esterification, blocking of hydroxyl groups with formaldehyde and methylation of brown alga biomass decreased the biosorption of AO7 dye. The results suggest that amine groups played a major role in adsorption of acid orange 7 at optimum pH. Furthermore, propylaminated biomass significantly increased the dye adsorption capacity as compared to the untreated alga.

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