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Chemical Engineering Journal 217 (2013) 329–336

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Acidic dye wastewater treatment onto a marine macroalga, *Nizamuddina zanardini* (Phylum: Ochrophyta)

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HIGHLIGHTS

- Acid Black 1 biosorption was studied onto marine macroalga.
- The maximum dye removal efficiency was observed at pH 2.0.
- Freundlich isotherm model showed the best fit with the equilibrium data.
- A decrease in particle size of *N. zanardini* biomass increased AB1 removal capacity.
- Addition of NaCl (0–40 g/L) to the dye solution increased dye removal efficiency.

ARTICLE INFO

Article history:
Received 25 August 2012
Received in revised form 5 November 2012
Accepted 6 November 2012
Available online 17 November 2012

Keywords:
Isotherm
Kinetic
Thermodynamic
Brown macroalga
Acid Black 1
Biosorption

ABSTRACT

Biosorption of Acid Black 1 (AB1) onto brown macroalgae, *Nizamuddina zanardinii*, was investigated. The effects of different parameters including pH, biomass loading, dye concentration, temperature, and salinity on the biosorption capacity were studies. The result at equilibrium was successfully described by the Freundlich model, and the estimated biosorption capacity was 29.79 mg/g. The kinetic of biosorption at different agitation speeds (70–180 rpm) and particle sizes (56–500 μm) were evaluated by pseudo-second-order, pseudo-first-order, and intraparticle diffusion kinetic models. The results showed that the pseudo-second-order model could be used as a successful model for the biosorption kinetics. Thermodynamics of sorption was investigated at different temperatures from 283 to 313 K. The negative values of Gibbs free energy, ΔG^0, and positive value of enthalpy, ΔH^0, confirm the possibility of the biosorption process and the spontaneous nature of the biosorption. A decrease in particle size of *N. zanardinii* biomass increased AB1 biosorption capacity. Furthermore, addition of NaCl (0–40 g/L) resulted in minor improvement in the dye biosorption. Role of different functional groups on the surface of biomass for biosorption of AB1 was investigated using FTIR.

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1. Introduction

Different industries such as textile, paper and pulp, printing, iron-steel, coke, petroleum, pesticide, paint, solvent, pharmaceutics, and wood preserving use dyes and pigments to color their products [1,2]. Dyes are the first pollutants that have been recognized in industrial wastewaters which influence water quality [3]. The discharged dyes can reduce light penetration in the wastewaters and affect photosynthetic activity in aquatic life [1,4]. Different dyes used in textile industries are very stable and difficult to be biodegraded [5,6]. They are severe contaminants and their removal is important in textile wastewater treatment [7]. Acid Black 1 is an amino acid staining diazo dye containing both NN and CC chromophore groups (pyrazolone dye). This synthetic acidic dye can be used for staining natural fibers such as cotton, wool silk, inks, paints, plastics and leather [8]. Due to adverse and harmful effects of AB1 on skin, eye, and respiratory system, it is necessary to entirely remove this dye from the wastewaters.

Several techniques have been employed for removal of dye from industrial effluents. The most commonly used methods are ozonation, photo-oxidation, electro-coagulation, adsorption (using activated carbon), froth flotation, reverse osmosis, ion exchange, membrane filtration, and flocculation [8–10]. However, these processes usually involve some disadvantages, including complicated

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http://dx.doi.org/10.1016/j.cej.2012.11.038

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procedures, formation of by-products, and high energy demands. Furthermore, they are not adaptable to a wide range of dye wastewaters [3,11].

Recently, there has been a growing interest in finding low-cost, easily obtainable, highly efficient, and environmentally benign alternatives to the current expensive methods [12,13]. Among the numerous techniques of dye removal from wastewaters, biosorption is one of the most efficient for removal of different types of dyes [14–17]. Biologically-originated materials such as banana pith, cotton waste, rice husk, teakwood bark, palm fruit bunch, decrystallized chitosan, microbial biomasses such as *Aspergillus niger* van Tieghem, *Rhizopus arrhizus* Fisher, *Cosmarium* sp., *Caulerpa scalpelliformis* (R. Brown ex Turner). C. Aghard and aquatic plants have been used as biosorbents to remove dyes from wastewaters [18,19]. Among these materials, several biosorbents showed extraordinary properties as biosorbents. Therefore, biosorption has been suggested as a practical and economically feasible treatment process.

Algae are widely available in both fresh and salt waters and have been found to be potential biosorbents [16]. Their biosorption capacity is attributed to their high surface area as well as high binding affinity [20]. Algal cell wall has several functional groups, e.g., hydroxyl, carboxylate, amino and phosphate, which played an important role in pollutant removal from wastewater [16]. The main substances of this type in brown alga are alginates, which usually constitute around 20–40% of the total dry weight, and some sulfated polysaccharides [21].

The proposed mechanism for removal of dye using algal biomass has been shown to be surface accumulation as well as bioaccumulation of dye ions [22].

In this study, the decolorization of AB1 contaminated water was investigated by brown macroalgae *Nizamuddina zanardinii* (Schiffner) P.C. Silva biomass. The effects of initial pH, biomass loading, and dye concentration as well as different salinity concentration on AB1 biosorption were investigated. Furthermore, kinetics and thermodynamics of biosorption for this system were studied.

2. Experimental

2.1. Dye solution

The chemical structure and general characteristics of AB1 (Alvan Sabet Corporation, Iran) used in this work is shown in Table 1. Different concentrations from 10 to 110 mg/L of AB1 were prepared by diluting 1000 mg/L stock of AB1 in distilled water. The concentration of dye was measured by spectrophotometery at 618 nm [23].

2.2. Biosorption preparation

The algal species, *N. zanardinii*, was acquired from Oman Sea coast of Chabahar, Iran in March, 2010. According to its morphology observations, it belonged to genus of *Sargassum* sp. and family of Sargassaceae. The alga was washed extensively with distilled water to remove dust and other particles. The clean biomass was sundried for 24 h, and then in the oven at 70 °C for 24 h. The dried biomass was crushed in a grinder and sieved to obtain three different particle sizes: 53–106, 106–250, and 250–500 μm. The powdered biomass was stored in an airtight container until use. The prepared biomass was used in all biosorption experiments in this study without any further chemical or physical treatments.

2.3. Biosorption study

Conventional biosorption methods have been used and adapted to the present study [24,25]. Biosorption experiments were conducted in batch mode of operation to investigate the effects of various parameters, i.e., pH (2–10), biosorbent loading (1–9 g/L), initial dye concentration (10–50 mg/L), contact time (2–90 min), temperature (283–313 K), particle size (53–500 μm), and NaCl addition (0.1–40 g/L), on the biosorption of AB1. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH. Then, the mixtures were incubated in a rotary shaker at 130 rpm and 27 ± 2 °C for 1 h. Blank experiments were also run under the same conditions in the absence of alga biomass. Samples were then filtered and the dye ions concentration in each sample was analyzed. Mass capacity of biosorption (q_e) was calculated from the difference between the initial and residual AB1 concentration as follows:

$$q_e = \frac{V(C_i - C_f)}{m} \quad (1)$$

where q_e is the dye sorption capacity (mg/g), C_i and C_f are the initial and equilibrium dye concentrations in the solution (mg/L) respectively, V is the solution volume (L), and M is the dry weight of biosorbent (g).

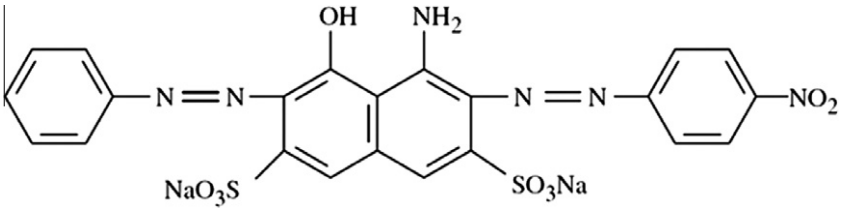
2.4. Equilibrium biosorption studies

Equilibrium experiments were carried out in 100 mL Erlenmeyer with 50 mL working volume in a rotary shaker at 130 rpm and 27 ± 2 °C for 1 h, which is sufficient to reach the equilibrium. Then, Langmuir, Freundlich, Doubinin–Radushkevich (D–R) and Temkin models were employed for biosorption isotherm modeling of the experimental data. Based on these assumptions, the final form of Langmuir model is given by [26]:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_0 (mg/g) indicates the monolayer sorption capacity of adsorbent and the Langmuir constant K_L (L/mg) is related to the energy of bisorption.

Table 1
General characteristics of Acid Black 1 [43].

Chemical structure	
C.I. number	20470
C.I. name	C.I. Acid Black 1
Class	Diazo
Ionization	Acidic
λ_{max} (nm)	618

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Freundlich expression is given by following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F is Freundlich constant (mg/g) and $1/n$ is an empirical parameter related to the biosorption intensity, which varies with the heterogeneity of the material. Another equation was used to study the isotherm proposed by D–R isotherm model which is based on Polanyi's biosorption potential theory and Dubinin's minipore filling theory:

$$q_e = q_s \exp(-\beta\varepsilon^2) \quad (4)$$

where q_e is the amount of adsorbed dye per unit weight of biomass (mol/g), q_s is the maximum biosorption capacity at equilibrium (mol/g), and β (mol^2/kJ^2) is the activity coefficient related to biosorption mean free energy, ε is the Polanyi potential which is given as follows [27]:

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \quad (5)$$

where R is the ideal gas constant (8.314 J/mol K), and T (K) is the absolute temperature. The constant β gives the mean free energy E (kJ/mol) of biosorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (6)$$

Also, Temkin isotherm model was used as follows:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (7)$$

where K_T (L mg^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy (L mg^{-1}) and b_T (g kJ mg^{-1} mol^{-1}) is the Temkin isotherm constant related to the heat of biosorption.

2.5. Biosorption kinetics

Experiments run to study biosorption kinetics were carried out in 100 mL Erlenmeyer containing 50 mL dye solutions in a rotary shaker at 130 rpm and 27 ± 2 °C for various time intervals (2–90 min). Liquid samples were taken at different time intervals, and filtered and analyzed for residual dye content. The kinetics data were analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models. The linear form of the pseudo-first-order rate equation can be defined as follows [28]:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (8)$$

where q_t is the amount of AB1 adsorbed up to time t (mg/g), q_e is the biosorption capacity in equilibrium (mg/g), k_1 is the rate constant of pseudo-first-order model (1/min), and t is the biosorption time (min). The pseudo-second-order model was represented in the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where k_2 is the rate constant (g/mg min). To calculate the values of k_2 and q_t at various AB1 concentrations (50–110 mg/L) and different pHs (2–11), the intercept and the slope of the linear plots of (t/q_t) verses t were obtained.

The intraparticle diffusion model is expressed as:

$$q_t = k_i t^{0.5} + c \quad (10)$$

where q_t (mg/g) is the amount of AB1 sorbed up to time t, c (mg/g) is the intercept, and k_i (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant.

2.6. Biosorption thermodynamics

Biosorption of AB1 by brown macroalga biomass was investigated at different temperatures (283, 298 and 313 K) under optimized conditions. Three thermodynamic parameters, i.e., Gibbs free energy changes (ΔG^0), enthalpy changes (ΔH^0), and entropy changes (ΔS^0) were used to determine the spontaneity of the biosorption process. The Gibbs free energy of the biosorption process, considering the biosorption equilibrium constant, was obtained from the following equation [29]:

$$\Delta G^0 = -RT \ln K_D \quad (11)$$

where $K_D(q_e/C_e)$ is the distribution coefficient. The ΔG^0 is related to the entropy change and heat of biosorption at constant temperature by the following equation [29]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

The value of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot between $\ln K_D$ and $1/T$.

2.7. FT-IR analysis

FT-IR spectra of the samples were recorded with a Jasco-680 (Japan) spectrometer at a resolution of 4 cm^{-1} through wavenumber range of 400–4000 cm^{-1}. Vibration bands were reported as wavenumber (cm^{-1}). FT-IR spectra of the samples were collected by making their pellets in KBr as a medium. The band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br).

3. Results and discussion

3.1. Effect of pH

The effect of initial pH, varying 2–10, on AB1 removal was studied (Fig. 1) at 30 mg/L initial concentration of AB1 using 1 g/L *N. zanardinii* biomass at 27 ± 2 °C for 60 min. The maximum dye biosorption of 58.05% was observed at pH 2. As can be seen in this figure, the biosorption capacity was decreased when the pH of solution was increased. Dye removal efficiency was decreased from 33.5% to 12.9% when pH increased from 3 to 4, while little biosorption was observed at pH of 4–10. This can be explained by the electrostatic interaction of AB1 with the negatively charged surface of the biomass. AB1 is an anionic dye that can be biosorbed on positively surface in acidic pH. Similar results have also been reported

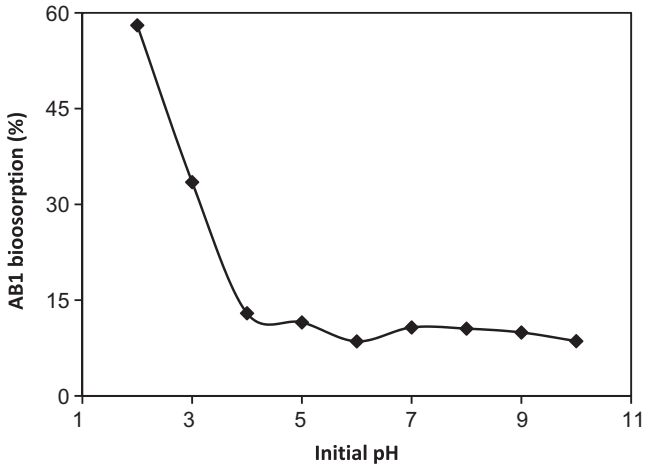

Fig. 1. Effect of different initial pHs of solution on biosorption of AB1 onto *N. zanardini* at 27 ± 2 °C, 30 mg/L of AB1 and 1 g/L of biomass.

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in the literature where the low pH was found to be favorable for Acid Black 1 sorption onto marine macrolage [30].

3.2. Effect of biomass loading

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 [31]. The effect of biomass dosage (1–9 g/L) on the biosorption of dye was investigated and the results are represented in Fig. 2. As can be seen in this figure, dye removal efficiency increased rapidly with increasing *N. zanardinii* biomass until it reached the value of 92.1% with the biomass content of 4 g/L. The reason for this observation is thought to be the fact that increasing algal biomass up to optimum points gives more surface area and more binding sites for sorption of the AB1 on the surface of the algae [8]. However, increasing biomass dosage to degrees higher than 4 g/L did not significantly increase the removal efficiency. At high sorbent dosage the probable aggregation of biosorbent particles limits the efficiency in the use of reactive groups.

3.3. Effect of dye concentration

The influence of dye concentration on the brown alga biosorption capacity (q_e) was studied by experiments carried out with 1 g L^{-1} biomass, pH 2, and different concentrations of AB1 from 10 to 50 mg L^{-1}. As shown in Fig. 3, the biosorption capacity was increased from 7.23 to 23.37 mg g^{-1} by increasing the initial dye concentration from 10 to 50 mg/L. The reason is the increase in the driving force, which is the concentration gradient, in the higher initial dye concentrations [2]. Furthermore, the contact of dye and biosorbent can increase in high concentrations of dye [32]. However, a saturation phenomenon should be expected at concentrations higher than those tested in this work, which usually lead to a constancy or even a decrease in sorption capacity and, at the same time, a decrease in sorption efficiency [24]. Higher sorption capacity for Acid orange II onto untreated (20.50–31.89 mg/g) and treated (20.30–45.47 mg/g) biomasses of *Stoechospermum marginatum* were reported by increasing the initial dye concentration from 30 to 90 mg/L[33].

3.4. Isotherm study

There are several isotherm equations for analysis of experimental biosorption equilibrium data. In this study, data were analyzed using four different isotherm equations, i.e. Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin models. The isotherm model

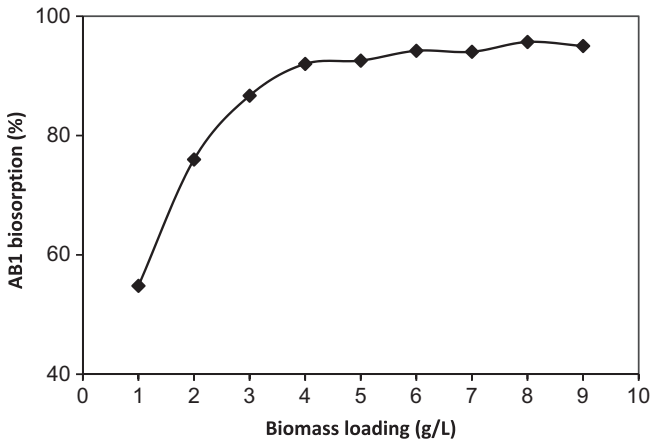

Fig. 2. Effect of different biomass dosages on biosorption of AB1 onto *N. zanardini* at 27 ± 2 °C, pH 2 and 30 mg/L of AB1.

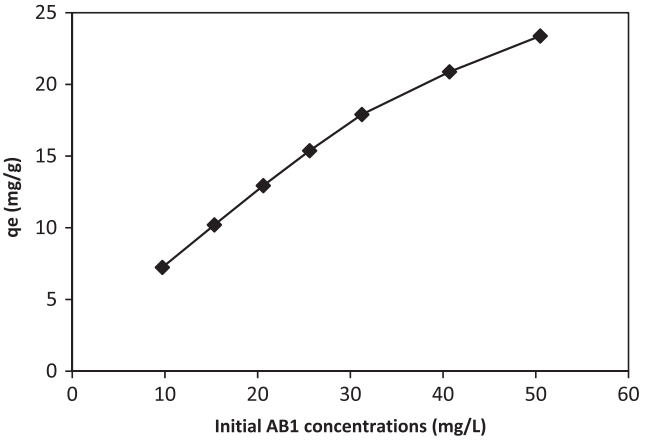

Fig. 3. Effect of different initial AB1 concentrations on biosorption of AB1 onto *N. zanardini* at 27 ± 2 °C, pH 2 and 1 g/L of biomass.

constants and the correlation coefficients (R^2) obtained for the models are presented in Table 2. The results suggested that the Freundlich isotherm model (Fig. 4) could successfully model the data ($R^2 > 0.99$). The model is among the best models for describing heterogeneous systems. This model suggests that biosorption energy exponentially decreases on completion of the sorptional centers of a biosorbent. The value of n (1.98) indicated the favorable biosorption under selected experimental conditions. The higher correlation coefficient predicts the multilayer biosorption of AB1 onto *N. zanardinii* biomass.

The E (kJ mol^{-1}) value gives information about biosorption mechanism, and more specifically its physical or chemical nature. If it lies between 8 and 16 kJ mol^{-1}, the biosorption process is controlled by a chemical mechanism, while for $E < 8$ kJ mol^{-1}, the biosorption process proceeds through a physical mechanism. The mean biosorption energy was found to be lower than 8 kJ/mol indicating that the biosorption of AB1 onto brown macroalgae biomass mainly proceeds by physically sorption.

3.5. Effect of contact time

A rapid biosorption process and establishment of equilibrium are important properties of a biosorbent for its application in wastewater treatment [34]. Biosorption of AB1 verses time up to 90 min was studied using 1 g/L biomass dosage for initial dye concentration of 30 mg/L at 27 ± 2 °C (Fig. 5). As can be seen in this figure, the dye was rapidly removed within the first 5 min, and thereafter the biosorption rate was gradually decreased and the sorption reached to equilibrium in about 90 min. In physical adsorption, most of the adsorbate are usually adsorbed within a short contact time [34]. In the biosorption mechanism, at the beginning, the dye molecules are adsorbed externally causing rapid increase of biosorption rate. When the external surface becomes saturated, the dye molecules are absorbed into the porous structure of the biomass [35]. On the other hand, the initial rapid phase may involve physical adsorption or ion exchange at cell surface and the subsequent slower phase may involve other mechanisms such as complexation, micro-precipitation or saturation of binding sites. Rapid adsorption of brilliant green using bagasse flay ash within the first 15 min has been reported [36]. The same results were observed in adsorption of Orange-G and Methyl Violet dyes by bagasse fly ash [34].

3.6. Kinetic study

Kinetics of biosorption explains the solute biosorption rate and gives the most important information to design biosorption

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Table 2
Isotherm constants of AB1 biosorption onto *N. zanardini* at different initial dye concentrations at 27 ± 2 °C, pH 2, and 1 g/L biomass.

	Langmuir model			Freundlich model			D–R model				Temkin model		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2	q_s (mg/g)	$k_{ad\times10}{}^5$ (mol^2/J^2)	E (kJ/mol)	R^2	b_T	A_T (L/mg)	R^2
N. zanardini	29.79	0.11	0.90	4.61	1.98	0.99	22.44	0.5	0.32	0.89	354.24	0.95	0.97

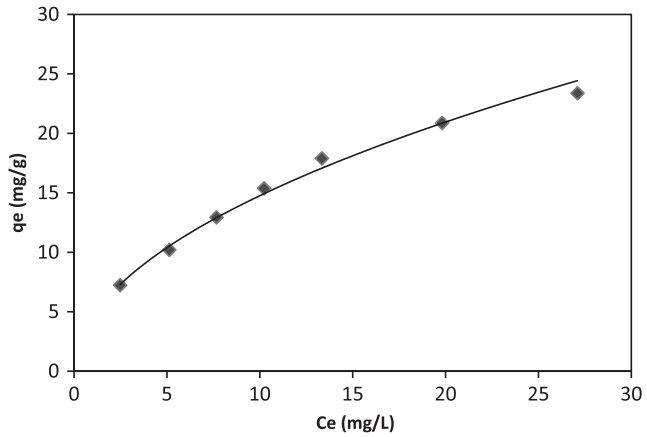

Fig. 4. Isotherm plots of biosorption of AB1 onto *N. zanardini* at 27 ± 2 °C, pH 2 and 1 g/L of biomass.

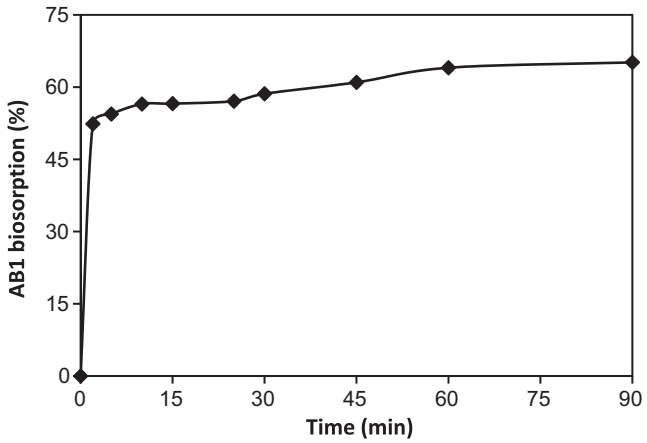

Fig. 5. Effect of contact time on biosorption of AB1 onto *N. zanardini* at 27 ± 2 °C, pH 2, 30 mg/L of AB1 and 1 g/L of biomass.

process [37]. In this work, in order to investigate the biosorption processes of AB1 onto the algal biomass, pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were examined. The model constants and correlation coefficients (R^2) were obtained for these models (Table 3). At all particle sizes and agitation speeds tested, intraparticle diffusion model was unable to describe the data well when compared with the other two models since R^2 values were low (between 0.62 and 0.95). The pseudo-first and second order values of R^2 suggested that the pseudo-second-order kinetic yielded a much better fit than pseudo-first-order (Table 3).

It is clear from Table 3 that coefficient of correlation (R^2) for pseudo-second-order model is higher and so this model could be used to describe the biosorption kinetics of AB1 onto *N. zanardinii* biomass. The maximum and minimum biosorption capacity values (q_2) obtained from pseudo-second-order model, were 28.57 and 20.83 (mg/g), respectively. The highest value of q_2 belongs to medium particle size (106–250 μm) at the least agitation speed (70 rpm); while the low biosorption capacity was observed in the largest particle size (250–500 μm) at maximum agitation speed (180 rpm). The minimum particle size tested showed the maximum biosorption of dye from aqueous solution. It may be related to different surface areas and binding sites. Larger particles provide the minimum number of binding sites exposed to the solution molecules and the smallest particle sizes provide largest surface area available for dye molecules to get bind. Also, since the equilibrium concentration depends on biosorbent particle size, the solute cannot interact with internal reactive groups [38].

Agitation speed is an important parameter in biosorption process, influencing the distribution of the solute in the bulk solution and the formation of the external boundary layer. The biosorption of AB1 was increased when the agitation speed was increased from 70 to 130 rpm followed by a slight decrease at 180 rpm. This indicated that 130 rpm is the optimum agitation speed for the biosorption process. Desorption of the sorbate at higher agitation speed might be the main reason for this observation. The effects of agitation speed on the kinetics of biosorption as well as the equilibrium biosorption capacity have been repeatedly found in biosorption [39]. Also, the decrease in biosorption capacity in high agitation speed can be attributed to the greater number of interactions between dye molecules to dye molecules and dye molecules to biosorbent particles. This increased number of interactions leads to desorption of dye molecules from the active binding sites of biosorbent [2].

3.7. Biosorption thermodynamics

Thermodynamic behavior of Acid Black 1 biosorption of onto *N. zanardinii* biomass was evaluated by the thermodynamic parameters including change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) of the sorption reaction. The obtained results are listed in Table 4. For a significant biosorption to occur, the free energy changes of biosorption, ΔG^0, must be negative. The calculated values of Gibbs free energy were −0.08, −0.063, and −1.02 kJ/mol for 283, 298, and 313 K, respectively. The negative value of ΔG^0 confirms the feasibility and spontaneity of the AB1 biosorption process. The increase in ΔG^0 values with the increase in temperature shows an increase in feasibility of biosorption at higher temperatures for all acidic dyes [40]. The positive value of change in enthalpy ΔH^0 shows that the biosorption process of AB1 is endothermic in nature. The positive value of change in entropy (ΔS^0) reflects the increased randomness at the solid/solution interface during the biosorption of acidic dye by *N. zanardinii* biomass. Some researchers have also obtained positive ΔH^0 and ΔS^0 in the biosorption of anionic dyes on other sorbents. Positive ΔH^0 and ΔS^0 were observed in sorption of brilliant green by bagasse fly ash [36] and uranyl and thorium ions by peat moss [40].

3.8. Effect of salinity

NaCl is the typical salt used to enhance the bath dye exhaustion. Therefore, in many wastewaters, a large volume of NaCl were accompanied with dyes that could influence their biosorption [41]. In this study, the effects of different concentrations of NaCl (0–40 g NaCl/L) on AB1 biosorption were evaluated (Fig. 6). In the absence of NaCl, the dye decolorization was 62.14%.

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Table 3
Kinetic parameters obtained from pseudo-first-order, pseudo-second-order, and intraparticle diffusion in different particle sizes and agitation speeds at 27 ± 2 °C, pH 2, 30 mg/L of AB1, and 1 g/L of biomass.

Models	0. 53–0.106 mm			0.106–0.250 mm			0.250–0.500 mm		
Agitation speed (rpm)	$k_{1\times10}{}^2$ (1/min)	q_1 (mg/g)	R^2	$k_{1\times10}{}^2$ (1/min)	q_1 (mg/g)	R^2	$k_{1\times10}{}^2$ (1/min)	q_1 (mg/g)	R^2
Pseudo-first-order									
70	3.0	2.38	0.97	3.4	2.82	0.97	3.0	2.89	0.99
130	3.0	2.34	0.97	2.5	2.54	0.99	6.5	2.73	0.91
180	3.2	2.49	0.96	2.9	3.11	0.97	3.4	3.29	0.96
	q_2 (mg/g)	$k_{2\times10}{}^2$ (g/mg min)	R^2	q_2 (mg/g)	$k_{2\times10}{}^2$ (g/mg min)	R^2	q_2 (mg/g)	$k_{2\times10}{}^2$ (g/mg min)	R^2
Pseudo-second-order									
70	27.57	2.92	0.99	23.81	1.51	0.99	22.72	1.86	0.99
130	28.57	4.08	0.99	25.00	3.81	0.99	23.81	2.52	0.99
180	27.01	5.26	0.99	21.73	6.22	0.99	20.83	7.68	0.99
	$k_{i\times10}{}^1$ (mg/g min$^{0.5}$)	C	R^2	$k_{i\times10}{}^1$ (mg/g min$^{0.5}$)	C	R^2	$k_{i\times10}{}^1$ (mg/g min$^{0.5}$)	C	R^2
Intraparticle diffusion									
70	8.85	21.21	0.89	10.26	14.87	0.95	9.15	15.05	0.91
130	8.31	22.46	0.86	5.86	20.05	0.88	2.57	22.09	0.62
180	6.07	22.47	0.83	5.98	17.16	0.64	3.72	17.68	0.75

Table 4
Thermodynamic constants of AB1 biosorption onto *N. zanardini* at different temperatures, pH 2, 30 mg/L of AB1, 1 g/L of biomass.

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
283	−0.08	8.81	31.50
298	−0.63		
313	−1.02		

Biosorption was increased from 65.14 to 72.24% by adding 0.1–40 g/L NaCl to the dye solution. In previous studies, different effects of salinity on acidic and basic dye removal have been observed; while the effect of salt concentration on the removal of Reactive Yellow 2 and Basic Red 5 has been negligible [41,42], removal of Basic Blue 9 has been increased by addition of NaCl [42]. For Acid Yellow 23, low concentration of salt (250 mg/L) resulted in 2% decrease in dye removal [43]. When NaCl concentration is increased, the salts can enhance the dissociation of dye molecules and thus, favor its precipitation on biomass, suggesting an aggregation mechanism that increases the biosorption capacity in the presence of ions, and in particular in presence of salts. Another reason is that increase in the ionic strength increases the positive charge of the surface, which in turn, increases the electrostatic interaction between anionic dye molecules and sorbent [44].

3.9. FT-IR study

The FT-IR analysis was conducted to obtain information on the possible interactions between the functional groups of biomass and AB1 ions. The FT-IR spectra of biomass before and after dye treatment are shown in Fig. 7. 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 cm^{-1} are assigned the asymmetric and symmetric C—H stretching of the aliphatic groups. The strong peaks at 1630 cm^{-1} were attributed to stretching vibration of carboxyl group (—C═O). The peak at 1384 is duo to —N═O stretching vibrations for the biomass. The bands observed at 1035–1109 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) [45,46].

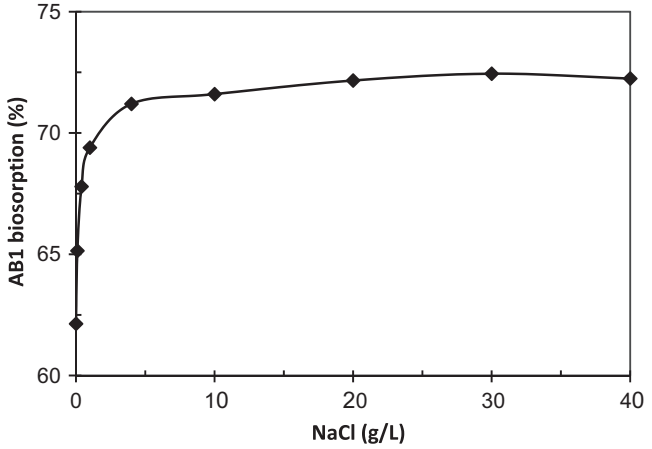

Fig. 6. Effect of different NaCl concentrations on biosorption of AB1 onto *N. zanardini* at 27 ± 2 °C, pH 2, 30 mg/L of AB1 and 1 g/L of biomass.

Comparison of dye loaded biomass with FTIR spectra of pure biomass displayed significant changes in some of the peaks. As can be seen in Fig. 7b, the shift and sharp reduction in the peak at 3419 cm^{-1} (74.5%) suggests the major role of —OH and —NH groups for AB1 biosorption onto *N. zanardinii* biomass. The significant reduction in the peak at 1635 cm^{-1} reflects the effect of carboxyl group upon binding of AB1 ions. The peaks were significantly shifted and decreased in the bands at 1109–1087 cm^{-1} and 1035–1026 cm^{-1} after dye treatment. These observations indicate that several functional groups on the surface of the biomass are responsible for binding of AB1 ions in the biosorption process. However, great shift and reduction of the peak at 3434–3419 cm^{-1} indicate that the hydroxyl and amine groups are the most important functional groups for biosorption of AB1 dye.

4. Conclusion

This study showed that the brown macroalga, *N. zanardinii*, can be efficiently used for Acid Black 1 removal. Maximum biosorption capacity was 29.97 mg/g at 27 ± 2 °C and pH 2 using 1 g/L algal biomass obtained within 90 min. Among the different parameters, pH

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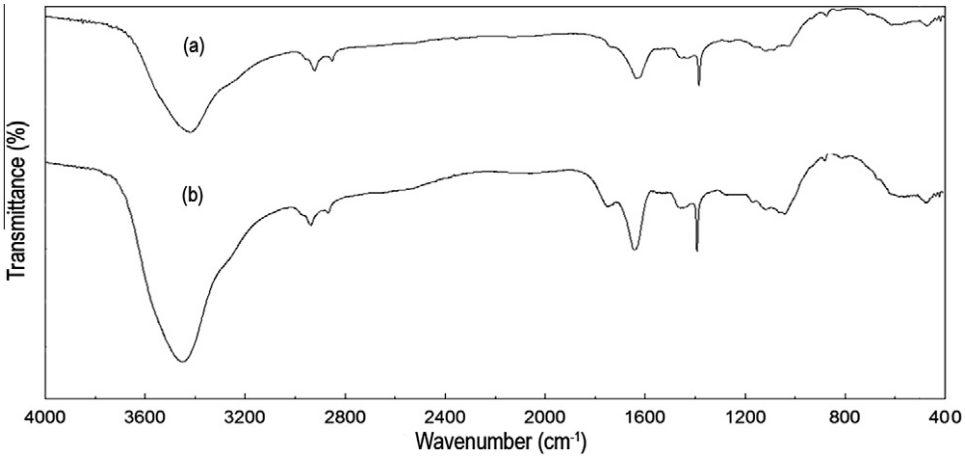

Fig. 7. FT–IR spectra of AB1 biosorption onto *N. zanardini* before treatment (a) and after 24 h of biosorption (b) at 27 ± 2 °C, pH 2, 30 mg/L of AB1 and 1 g/L of biomass.

highly affected the biosorption capacity. The kinetics of AB1 biosorption by the *N. zanardinii* biomass can be described by the pseudo-second-order model. Biosorption isotherm of this system was described by the Freundlich model. Hydroxyl and amine groups on the surface of biomass were the most important functional groups for biosorption of AB1 dye.

Acknowledgments

This work was financially supported by Isfahan University of Technology, Isfahan Water and Sewage Company and Isfahan Municipality. Thanks should also go to Bairam Mohammad Gharanjic (Chabahar, Oman Sea) for the collection and classification of the alga species.

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