Biosorption of food dyes onto Spirulina platensis nanoparticles: Equilibrium isotherm and thermodynamic analysis

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The biosorption of food dyes FD&C red no. 40 and acid blue 9 onto Spirulina platensis nanoparticles was studied at different conditions of pH and temperature. Four isotherm models were used to evaluate the biosorption isotherm and the thermodynamic parameters were estimated. Infra red analysis (FT-IR) and energy dispersive X-ray spectroscopy (EDS) were used to verify the biosorption behavior. The maximum biosorption capacities of FD&C red no. 40 and acid blue 9 were found at pH 4 and 298 K, and the values were 468.7 mg g⁻¹ and 1619.4 mg g⁻¹, respectively. The Sips model was more adequate to fit the equilibrium experimental data (R² > 0.99 and ARE < 5%). Thermodynamic study showed that the biosorption was exothermic, spontaneous and favorable. FT-IR and EDS analysis suggested that at pH 4 and 298 K, the biosorption of both dyes onto nanoparticles occurred by chemisorption.

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1. Introduction

Many industries, especially food and textile industries often use dyes and pigments to color their products. As a result, about 10–20% of the dyes are lost during the manufacturing and process, producing large amounts of wastewater (Gao et al., 2011). The dye-containing wastewater discharged from the industries can adversely affect the aquatic environment by impeding light penetration. Moreover, most of the dyes are toxic, carcinogenic and harmful to human health (Yang et al., 2011). This manner, many techniques have been developed to dye removal, such as, flocculation combined with flotation, electroflocculation, membrane filtration, electrokinetic coagulation, electrochemical destruction, ion-exchange, irradiation, precipitation and ozonation. However, these technologies are generally ineffective in color removal, and they are expensive and less adaptable to a wide range of dye wastewaters (Srinivasan and Viraraghavan, 2010). Biosorption has emerged as an alternative eco-friendly technology to dye removal from aqueous solutions. This technology has several advantages, such as, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions (Aksu, 2005; Aksu and Tezer, 2005; Patel and Suresh, 2008; Srinivasan and Viraraghavan, 2010).

Biosorption refers to the ability of certain biomaterials to bind and concentrate toxic pollutants from even the most dilute aqueous solutions (Aksu, 2005). In the case of dyes removal, many biosorbents are reported by the literature, such as, chitosan (Dotto and Pinto, 2011a), fungi (Patel and Suresh, 2008; Russo, 2010), algae (Aksu and Tezer, 2005; Çelekli and Geyik, 2011) and bacteria (Yang et al., 2011). Spirulina platensis were successfully employed to remove cadmium (Solisio et al., 2008; Çelekli and Bozkurt, 2011), cooper (Çelekli et al., 2010; Fang et al., 2011), chromium (Gokhale et al., 2008, 2009), lead (Gong et al., 2005; Seker et al., 2008) and nickel (Seker et al., 2008; Çelekli and Bozkurt, 2011). Thus, there is a great number of studies related to metals biosorption by S. platensis, however its use to dye removal is very restricted and rarely investigated (Çelekli et al., 2009).

The blue–green algae S. platensis have availability in large quantities, it is largely cultivated throughout worldwide and its annual production is about 2000 ton (Çelekli and Yavuzatmaca, 2009; Çelekli et al., 2010; Costa and Morais, 2011). Its biomass contain a variety of functional groups such as carboxyl, hydroxyl, sulfate, phosphate and other charged groups which can be responsible for dye binding (Seker et al., 2008; Çelekli and Bozkurt, 2011; Çelekli and Geyik, 2011; Fang et al., 2011). However, the totality of these groups is not accessible in the biomass natural form. This manner, the preparation of the nanoparticles from biomass is a good way to increase the accessible biosorption sites of the biomass. In addition, recent advances in the field of nanotechnology show that ultra-fine biosorbents are a good alternative to dye removal (Cheung et al., 2009; Inbaraj and Chen, 2011).
2. Methods

2.1. Dyes

The commercial food dyes FD&C red no. 40 and acid blue 9 from aqueous solutions. The effects of pH and temperature on the equilibrium isotherm and thermodynamics were investigated. Infra red analysis (FT-IR) and energy dispersive X-ray spectroscopy (EDS) were carried out to verify the biosorption behavior.

2.2. Culture conditions and drying of S. platensis biomass

S. platensis strain LEB-52 (Costa et al., 2004) was cultivated in a 450 L open outdoor photo-bioreactors, under uncontrolled conditions, in the south of Brazil. During these cultivations, water was supplemented with 20% Zarrouk synthetic medium (Zarrouk, 1966) containing (g.L-1): NaHCO3, 16.8; NaNO3, 2.5; K2HPO4, 0.5; K2SO4, 1.0; NaCl, 1.0; MgSO4·7H2O, 0.2; CaCl2, 0.04; FeSO4·7H2O, 0.01; EDTA, 0.08 and micronutrients. At the end of cultivation, the biomass was recovered by filtration, washed with distilled water and pressed to recover the biomass with a moisture content higher than 85%. The dyes wavelength is constant with the pH. Dis- solved oxygen (DO) was measured before and after the agitation (Mars, MB10, Brazil).

2.3. Preparation and characterization of nanoparticles

The S. platensis nanoparticles were obtained by a mechanical method (Anton et al., 2008). The dried biomass was ground by a mill (Wiley Mill Standard, No. 03, USA) and it was sieved until the discrete particle size ranged from 68 to 75 μm. The sieved biomass (50 mg) was added in distilled water (90 mL) and the pH was corrected (4), (6), and (8) using 10 mL of a buffer disodium phosphate/citric acid solution (0.1 mol L-1). After, the suspension was agitated (Dremel, 1100-01, Brazil) at 10,000 rpm for 20 min. These conditions were found by preliminary tests, and the size distribution was not influenced by pH.

The size distribution and average diameter of the nanoparticles were evaluated in suspension by dynamic light scattering (DLS) (Bruce and Pecora, 2000). The dynamic light scattering equipment was constituted by a laser (Spectra-Physics, 127, USA) coupled to a goniometer (Brookheaven, BI-200M, USA) and a digital correlator (Brookheaven, BI-9000AT, USA). The nanoparticles before and after the biosorption process (in the more adequate condition) were characterized by energy dispersive X-ray spectroscopy (EDS) (Pioneer, S2 Ranger, Germany) (Moghaddam et al., 2010) and infra red analysis (FT-IR) (Prestige 21, the 210045, Japan) (Sakkayawong et al., 2005). The zero point charge (pHzpc) of S. platensis nanoparticles was determined using the eleven points experiment, according Hao et al. (2004): Eleven flasks with 50 mL of a suspension containing 25 mg of nanoparticles (initial pH values in the range from 1.0 to 12.0, these were adjusted with HCl and NaOH) were agitated at 100 rpm using a Wagner agitator (Fanem, 315 SE, Brazil) until the equilibrium (about 24 h). The pH values were measured before and after the agitation (Mars, MB10, Brazil).

2.4. Equilibrium experiments

The equilibrium biosorption isotherms were carried out by batch conditions at different values of pH (4), (6), and (8) and temperature (298, 308, 318 and 328 K). These values were determined from the literature and preliminary tests. According to Srinivasan and Viraraghavan (2010) the pH and temperature play an important role in dye biosorption onto algal biomass. Firstly, 90 mL of a suspension containing 50 mg of nanoparticles had the pH corrected (pH 4, 6 and 8) through the 10 mL of buffer disodium phosphate/citric acid solution (0.1 mol L-1), which did not present interaction with the dyes. In these suspensions, were added 100 mL of dye solutions with different concentrations (from 100 to 1300 mg L-1); this manner the initial biosorbtion concentration was 250 mg L-1. After, the suspensions were placed in flasks and agitated at 100 rpm using a thermostated type Wagner agitator (Fanem, 315 SE, Brazil). Samples were analyzed every 8 h. The equilibrium was considered attained when the dye concentration in the liquid did not present difference between three consecutive measures. The biomass and biosorbed dyes were removed of the liquid through a filtration with Whatmann Filter Paper No. 40, which did not present interaction with the dyes, and the dye concentration was determined by spectrophotometry (Quimis, Q108, Brazil) (Piccin et al., 2009). The experiments were carried out in replicate (three times for each experiment) and blanks were performed.

The equilibrium biosorption capacity (qe) was calculated as follows (Piccin et al., 2009):

\[ q_e = \frac{C_0 - C_e}{e} \]  

where \( C_0 \) is the initial dye concentration in liquid phase (mg L-1), \( C_e \) is the dye concentration in liquid phase at equilibrium (mg L-1), \( e \) is biosorbent dosage (g) and \( V \) is the volume of suspension (L).
2.5. Isotherm models

Equilibrium biosorption isotherm is the most important design parameter that describes how the adsorbate interacts with the biosorbent (Inbaraj and Chen, 2011). In order to obtain information about the interactions between food dyes and _S. platensis_ nanoparticles, Langmuir, Freundlich, Dubinin–Radushkevich and Sips models were fitted to the experimental data.

The Langmuir isotherm is derived assuming a uniform surface with finite identical sites and monolayer adsorption of the adsorbate (Gokhale et al., 2008). The Langmuir isotherm is given by the relation:

\[ q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \]  

where \( q_m \) is the maximum monolayer biosorption (mg g\(^{-1}\)) and \( k_L \) is the Langmuir constant (L mg\(^{-1}\)).

Another essential characteristic of the Langmuir isotherm can be expressed by the separation factor or equilibrium factor (\( R_L \)) (Piccin et al., 2009), as follows:

\[ R_L = \frac{1}{1 + k_L C_0} \]  

The Freundlich adsorption isotherm gives the empirical relation between \( q_e \) and \( C_e \) (Gokhale et al., 2009). The Freundlich isotherm is given by the relation:

\[ q_e = k_F C_e^{1/n} \]  

where \( k_F \) is the Freundlich constant (\((\text{mg g}^{-1})(\text{mg L}^{-1})^{-1/2}\)) and \(1/n\) is the heterogeneity factor.

Another equation used in the analysis of isotherms was proposed by Dubinin and Radushkevich (Kavitha and Namasivayam, 2007):

\[ q_e = q_s \exp(-B \varepsilon^2) \]  

where \( q_s \) is the D–R constant (mg g\(^{-1}\)) and \( \varepsilon \) can be correlated:

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

The constant \( B \) (mol\(^2\) kJ\(^{-2}\)) gives the mean free energy \( E \) (kJ mol\(^{-1}\)) of adsorption per molecule of adsorbate when it is transferred to the surface of the solid from infinity in the solution (Kavitha and Namasivayam, 2007), and can be computed using the following relationship:

\[ E = \frac{1}{\sqrt{2B}} \]  

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms (Cardoso et al., 2011):

\[ q_e = q_m (k_C C_e)^m \]  

where \( q_m \) is the maximum monolayer biosorption (mg g\(^{-1}\)), \( k_C \) is the Sips constant (L mg\(^{-1}\)) and \( m \) is the exponent of the Sips model.

The isotherms parameters were determined by nonlinear regression, using the software Statistica 6.0 (Statsoft, USA). The fit quality was measured according to the coefficient of determination \( (R^2) \) and average relative error (ARE) (Piccin et al., 2009):

2.6. Thermodynamic study

In order to evaluate the biosorption thermodynamic behavior, the values of Gibbs free energy change (\( \Delta G \)), enthalpy change (\( \Delta H \)) and entropy change (\( \Delta S \)) were estimated as follows (Milonjic, 2007):

\[ \Delta G = -RT \ln (55.5 K_D) \]  

\[ \ln(55.5 K_D) = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \]  

where \( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the temperature (K), \( K_D \) is the thermodynamic equilibrium constant (L mol\(^{-1}\)) and 55.5 is the number of moles of water per liter of solution. The \( K_D \) values were estimated from the parameters of the best fit isotherm model and the molecular weight of the dyes (Cardoso et al., 2011).

3. Results and discussion

3.1. Characterization of _S. platensis_ nanoparticles

The _S. platensis_ nanoparticles were characterized in relation to the size distribution (Fig. 2a), autocorrelation function (Fig. 2b)
and zero point charge (Fig. 2c). The EDS and FT-IR results are presented and discussed in Section 3.2.

In Fig. 2(a) it can be observed that S. platensis nanoparticles in suspension showed a normal and uniform size distribution in the range from 120 to 350 nm. The average diameter of the nanoparticles was 210 nm (obtained from dynamic light scattering). Nanoparticles are commonly described as solid colloidal particles, ranging in size from 10 nm to 1 μm (Anton et al., 2008). In addition DLS showed that the autocorrelation function was unimodal (Fig. 2b) and the polydispersity index was 0.150, confirming a little variation in the nanoparticles size.

The plot of pH initial versus pH final of the S. platensis nanoparticles in suspension are showed in Fig. 2c. This figure shows that the pH_zpc of the S. platensis nanoparticles was seven. When the pH of the suspension is lower than seven, the surface of the S. platensis nanoparticles gets positively charged and the surface of the S. platensis is negatively charged at pH values higher than seven. The zero point charge (pH_zpc) of the biosorbent is one way to understand the biosorption mechanisms (Çelekli et al., 2010).

3.2. Biosorption isotherms

The biosorption isotherms curves at different conditions were showed in Fig. 3 (FD&C red no. 40) and Fig. 4 (acid blue 9). The biosorption isotherms curves of both dyes were characterized by an initial step with increase in biosorption capacity followed by a convex shape. The initial step indicates a great nanoparticles-dyes affinity and numerous readily accessible sites. The convex shape suggests the formation of a monomolecular layer of the dyes on the nanoparticles surface.

The comparison between Figs. 3 and 4 show that in all conditions, the biosorption capacity of FD&C red no. 40 was lower than acid blue 9. This occurred, probably, because acid blue 9 pK_a (5.6 and 6.6) is lower than FD&C red no. 40 pK_a (11.4), facilitating the dissociation of D-SO_3Na and its conversion to D-SO_. In addition, acid blue 9 had more sulfonated groups than FD&C red no. 40 (Fig. 1). Some researches found that the sulfonated groups of the anionic dyes are responsible to the dye–biosorbent interactions (Patel and Suresh, 2008; Cheung et al., 2009; Dotto and Pinto, 2011a; Gao et al., 2011).

As shown in Figs. 3 and 4 (FD&C red no. 40 and acid blue 9, respectively), the biosorption capacity of S. platensis nanoparticles increased when pH was decreased from 8 to 4, and reached maximum values at pH 4. Then in the experimental conditions, the best pH for biosorption of both dyes onto S. platensis nanoparticles was 4 (Figs. 3a and 4a). According to Cheung et al. (2009), the acid dyes are first dissolved in aqueous solution, and the sulfonate groups of acid dyes are dissociated (D-SO_3Na), and they are converted to anionic dye ions (D-SO_2^-). Also, at pH 4 and 6 the nanoparticles surfaces are positively charged and at pH 8 the surface could be negatively charged (according to Fig. 2c). This manner, the pH decrease leads to an increase in the positively charged groups on the nanoparticles surface, and electrostatic attraction occurs between the dyes sulfonated groups and functional groups on the surface. Similar behavior was found by Aksu and Tezer (2005) in the biosorption of reactive dyes onto Chlorella vulgaris. They concluded that at lower pH values functional groups such as amines or imidazoles in the biomass were protonated, and the biosorption proceeded thought electrostatic attractions between negatively charged dye anions and positively charged cell surface.

It was observed in Figs. 3 and 4 (FD&C red no. 40 and acid blue 9, respectively), that the biosorption capacity of both dyes onto S. platensis nanoparticles was increased with the temperature decrease. In the temperatures of 298 and 308 K, a small difference was observed. At 318 and 328 K the biosorption capacity was strongly decreased. The best temperature for biosorption of both dyes onto S. platensis nanoparticles was 298 K. The temperature increase causes an increase in the solubility of the dyes (Crini and Badiani, 2008), so, the interaction forces between the dyes and the solvent become stronger than those between dyes and nanoparticles. In addition, according to Aksu (2005), at temperatures above 318 K can occurs the damage of sites on the surface of biomass and, consequently a decrease in the surface activity. Similar behavior was observed by Piccin et al. (2009) in the adsorption of FD&C red no. 40 onto chitosan.
The isotherm models nominated Langmuir (Eq. (2)), Freundlich (Eq. (4)), Dubinin–Radushkevich (Eq. (5)) and Sips (Eq. (8)) were used. The isotherm parameters of FD&C red no. 40 and acid blue 9 biosorption onto *S. platensis* nanoparticles at different conditions were showed in Tables 1 and 2, respectively. The values of the coefficient of determination ($R^2 > 0.99$) and average relative error (ARE < 5%) presented in Tables 1 and 2 show that the Sips model was more adequate to represent the equilibrium experimental data. The ’$m$’ values obtained from the Sips model ($m$) indicated a heterogeneous biosorption process and the multiple biosorption sites on the *S. platensis* nanoparticles.

The maximum biosorption capacities ($q_m$) obtained from the Sips model were 468.7 mg g$^{-1}$ for the FD&C red no. 40 and 1619.4 mg g$^{-1}$ for the acid blue 9, at pH 4 and 298 K. Aksu and Tezer (2005) in the biosorption of reactive dyes onto *C. vulgaris* found maximum biosorption capacities of 555.6 mg g$^{-1}$, 196.1 mg g$^{-1}$ and 71.9 mg g$^{-1}$ for the dyes, remazol black, remazol green and remazol golden yellow, respectively. Patel and Suresh (2008) obtained values from 65 mg g$^{-1}$ to 106.4 mg g$^{-1}$ in the biosorption of reactive black 5 onto *Aspergillus foetidus*. Yang et al. (2011) were found 411.53 mg g$^{-1}$ in the biosorption of Congo red by inactive *Penicillium YW 01* biomass.

3.3. Thermodynamic analysis

The biosorption thermodynamic parameters were estimated from the Sips parameters, as reported in the literature (Cardoso et al., 2011). The values of $\Delta G$, $\Delta H$ and $\Delta S$ in all experimental conditions were showed in Table 3.

In Table 3, negative values of $\Delta G$ for both dyes indicate that the biosorption was a spontaneous and favorable process, whereby no energy input from outside of the system is required. Negative $\Delta H$ values confirm the exothermic nature of the biosorption process. The negative $\Delta S$ values indicate that randomness decreases at the solid-solution interface during the biosorption of both dyes by *S. platensis* nanoparticles. The negative $\Delta H$ and $\Delta S$ values suggest that enthalpy contributes more than entropy in negative $\Delta G$ values. These results were in accordance with Srinivasan and Viraraghavan (2010), that reported the biosorption onto algae, in most of cases, is an exothermic process.

3.4. EDS and FT-IR results

In order to verify the biosorption behavior and the possible interactions of FD&C red no. 40 and acid blue onto *S. platensis* nanoparticles, EDS and FT-IR analysis were carried out before and after the biosorption process in the more adequate condition (298 K and pH 4).

The EDS analysis (figure not shown) showed that the major elements on the surface of the *S. platensis* nanoparticles before biosorption were C (54.0%), N (33.9%), O (9.2%), P (1.8%) and S (1.1%). After biosorption process the percentage values of C, O, and S were increased, and consequently, the percentages of N and P were decreased. This occurred due to the trapped dye molecules which contain aromatic rings and sulfonic groups, thus shown strong interaction between dyes and nanoparticles. In addition, the increases of C (59.5%) and S (3.1%) in the nanoparticles loaded with FD&C red no. 40 were lower than the increases of C (67.0%) and S (4.4%) in the nanoparticles loaded with acid blue 9. This occurred, because acid blue 9 had more sulfonated groups and aromatic rings than FD&C red no. 40 (Fig. 1).

The FT-IR spectrum of *S. platensis* nanoparticles (Supplementary material (a)) showed several major intense bands, around 3370, 2920, 2859, 1659, 1535, 1224, 1149, 1021, 852 and 762 cm$^{-1}$. The O–H bond stretching mixed with NH$_2$ group can be observed at 3370 cm$^{-1}$. The peaks 2920 and 2859 cm$^{-1}$ are relative to an asymmetric and symmetric stretching of CH$_2$ groups. The scissor bending of NH$_2$ group can be observed at 1659 and 1535 cm$^{-1}$. The bands of 1224, 1149, 1021 cm$^{-1}$ could be attributed to a C–N stretch of amide or amine. According Çelekli et al. (2010), the adsorption peaks in the region 750–900 cm$^{-1}$ could be attributed to –P–O, –S–O, and aromatic –CH stretching vibrations. After biosorption of FD&C red no. 40 (Supplementary material (b)) and acid
blue 9 (Supplementary material (c)) some shifts in the wave numbers were observed. The peak 3370 cm⁻¹ is associated, the biosorption process then proceeded due to the electrostatic groups of the dyes from aqueous solutions. Srinivasan and Viraraghavan (2010) reported that the functional groups such as hydroxyl and amino on the surface of algal biomass are considered to be responsible for sequestration of dyes from aqueous solutions.

On the basis in the EDS and FT-IR analysis it can be inferred that the biosorption of both dyes onto S. platensis nanoparticles occurred by chemisorption. The possible biosorption mechanism is presented as follows: under acidic conditions, hydrogen atoms (H⁺) in the solution could protonate the amine and hydroxyl groups of S. platensis nanoparticles, in addition, FD&C red no. 40 and acid blue 9 were dissolved and its sulfonate groups were dissociated, the biosorption process then proceeded due to the elec-
trostatic interactions between dyes sulfonated groups and nanoparticles protonated groups. Electrostatic interactions between algal functional groups and dyes sulfonated groups were demonstrated by other workers (Aksu, 2005; Srinivasan and Viraraghavan, 2010).

4. Conclusion

*S. platensis* nanoparticles were used as biosorbent to removal FD&C red no. 40 and acid blue 9 from aqueous solutions. The equilibrium isotherms were carried out at pH of 4, 6 and 8 and temperature of 298, 308, 318 and 328 K. The maximum biosorption capacities were 468.7 mg g⁻¹ for the FD&C red no. 40 and 1619.4 mg g⁻¹ for the acid blue 9, at pH 4 and 298 K. The Sips model was the best to represent the equilibrium experimental data. The biosorption was exothermic, spontaneous and favorable. At pH 4 and 298 K, the biosorption of both dyes onto nanoparticles occurred by chemisorption.

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Appendix A. Supplementary data


References


