Treatment of textile industry effluents using orange waste: a proposal to reduce color and chemical oxygen demand
Carlos Eduardo de Farias Silva, Andreza Heloiza da Silva Gonçalves and Ana Karla de Souza Abud

ABSTRACT
Various agricultural residues have been tested as biosorbents due to their low cost, high surface area, and favorable surface chemistry. In this work, a sweet orange albedo was tested as a biosorbent for treatment of real textile effluents. The orange albedo powder was prepared by drying the residue at 50°C and milling to 30 mesh, and then used for dye adsorption from an alkaline (pH = 10.71) effluent. The adsorption process was studied in batch experiments at 30°C by measuring color removal and chemical oxygen demand (COD). The color removal was found not to be significantly altered when the effluent was used in its raw state, while COD increased probably due to albedo degradation. For the effluent diluted to 60% (Veﬄuent / VH2O), color and COD removal percentages of approximately 89% were obtained. It was found that pH played a very significant role on the adsorption process, as the treated albedo displayed a relative pH_PZC* of 4.61, and the highest dye removal efficiencies were reached at pH lower than 2. The COD was strongly influenced by the effluent dilution. The effectiveness in eliminating color and COD shows that orange albedo can be potentially used as a biosorbent to treat textile wastewater.

Key words | biosorption, citrus residue, dye, removal

INTRODUCTION
Brazil is one of the worldwide largest fruit producers, with an annual production superior to 40 million fruits by tonnage, which accounts for 6% of the global production (Andrigueto et al. 2015). A portion of 50% of fruits produced in Brazil is processed into juices, pulps, jams, etc., to supply the national fruit market over long distances and between post-harvest seasons. Nevertheless, fruit processing in Brazil usually results in a large amount of residues which have been traditionally destined to animal feed (ABF 2015). These residues contain high pollutant content to air, soil, and water bodies; hence their disposal can lead to adverse impacts to ecosystems (Salleh et al. 2011).

Agricultural residues are lignocellulosic materials mainly composed of three high molecular weight macromolecules: cellulose, lignin, and hemicellulose (Salleh et al. 2011). They have the advantage of being renewable, largely available and cheaper than other biosorbents commercially used for environmental protection.

Alagoas is a traditionally agricultural state with a large production of biomass in Brazil. It is considered the largest producer of sweet orange (Citrus sinensis Osbeck) at Brazilian northeast, concentrating about 90% of its production at the Santana do Mundaú region, making the consumer market of iced orange continuously increase. Some industries remove the citrus peel before the juice extraction process in order to obtain the essential oil, which can be used as an ingredient of the own juice, to restore the orange taste after concentration, or it is exploited as a high added-value product by cosmetic/pharmaceutical/food industries, making albedo the main residue from the citrus industry.

Textile industry consumes vast amounts of water and chemicals, specifically to perform dyeing and finishing processes. Unfortunately, the exact amount of textile dyes consumed worldwide is unknown, being estimated in approximately 10,000 tons per year. Regarding the amount
of dye discharged into the environment, losses of 1 to 2% and 1 to 10% at the production step and for usage, respectively, are estimated. For reactive dyes, which are mostly used for cotton dyeing in Brazil, the discharged amount could be estimated in about 4% (Forgacs et al. 2004; Schimmel et al. 2010). Liquid textile effluents are generally produced from water used in the washing and cooling steps, where the washing step accounts for 60 to 70% of total water volume used by the textile industry (Souza et al. 2007). Between 200 and 400 L of water is consumed in order to produce one kg of tissue (Robinson et al. 2000).

The low biodegradability of dyes as a function of their mutagenic, carcinogenic and teratogenic effects makes conventional biological treatments not a very effective operation to eliminate dyes from textile wastewater (Moreira et al. 2002). Thus, biosorption has been recently studied as a simple and high efficient process for textile effluent treatment.

Biosorption is the use of biomass in adsorptive processes. It is advantageous not only for presenting low cost and large efficiency, but also for adding value to agricultural residues. Biomass is mostly comprised of macromolecules such as cellulose, lignin, proteins and pectins, whose surface chemical groups act as binding sites in adsorption processes (Volesky 2007; Sud et al. 2008). Several adsorbents from agricultural solid residues have been studied, for instance, active carbon from sugarcane bagasse, coconut rusk, rice straw, and citric residues, among others (Aksu 2005; Volesky 2007; Salleh et al. 2011).

In this work, a sweet orange residue was characterized and tested as a biosorbent for treatment of real textile effluents. The dye adsorption process was studied by means of color removal and chemical oxygen demand (COD) determinations with the aim to establish optimized treatment conditions.

**METHODS**

**Preparation and characterization of orange albedo**

Lima acidless sweet oranges were initially peeled and crushed in order to eliminate their juice. The remaining orange portion, well-known as orange albedo, was cut up and disinfected with sodium hypochlorite solution (100 ppm) for 15 min. The treated albedo was then dried in an air circulating oven at 50 °C until it was a constant weight, and then pulverized in a 30 mesh using a Wyllie-type milling, and stored into a hermetic plastic bag at room temperature.

The surface physical morphology of the orange albedo was observed on a scanning electron microscope (Shimadzu SSX-550) and also characterized by Fourier transform infrared spectroscopy (FTIR), in the range from 4,000 to 400 cm⁻¹ in order to verify the main functional groups of the albedo particles structure.

Centesimal composition analyses were carried out by quantifying lipid (L), protein (P), moisture (U), ash (C), fiber (F) and pectin (PEC) contents following the Adolf Lutz standard procedures (ALI 2008) with some modifications (Gama et al. 2005; Silva et al. 2015). The theoretical carbohydrate content (Ca) was calculated by Equation (1).

\[
Ca = 100 - [L + P + U + C + F]
\]  

(1)

**Characterization of textile effluent**

Dye concentrations were determined using a UV-mini 1240 Shimadzu spectrophotometer from effluent dilutions from 0 to 90% (\(V_{\text{effluent}}/V_{1,0} \)) where the raw effluent was considered as the concentration of 100%. Additionally, the effluent was characterized in terms of its pH, total solids content (dry matter content) and COD (APHA 1995). In order to evaluate the effluent color, a scanning was performed in the wavelength range 410–750 nm, as indicated by DIN EN ISO 7887 (2011). The dye concentration in the effluent was then obtained by absorbance measurements at the maximum absorption wavelength (\(\lambda_{\text{max}}\)). Dye concentration (\(Q\)) and dye removal percentage (\(\%\text{Rem}\)) were calculated by Equations (2) and (3), respectively.

\[
Q(\%) = \frac{Abs \times Fc \times D}{100}
\]  

(2)

\[
\%\text{Rem} = \frac{(Q_i - Q_f) \times 100}{Q_i}
\]  

(3)

where \(Abs\) is the absorbance at 672 nm, \(Fc\) is the effluent calibration curve factor at different dilutions, \(D\) is the dilution value, \(Q_i\) is the initial dye concentration (OD₆₇₂nm), and \(Q_f\) is the final dye concentration (OD₆₇₂nm).

**Preliminary adsorption study**

Dye adsorption studies were preliminarily performed by a finite batch technique using the raw effluent and 1% albedo content (\(m_{\text{adsorbent}} / V_{\text{effluent}} \)). The experiments were conducted in 100 mL glass flasks, using an incubator shaker operating at 100 rpm and 30 °C. Aliquot parts were
taken at each 5 min, separating the effluent and biomass by simple filtration using qualitative cellulose filters for subsequent UV-Vis absorbance measurements. COD determinations were evaluated at each 5 min in a period between 0 and 30 min.

**Evaluation of effluent dilution and biomass concentration in acidic pH**

In order to improve the efficiency of color and COD removal, batch experiments were carried out. The first set of experiments involved the raw effluent (100%), changing the biomass concentration (0.5, 1.0 and 2.5%) and their respective levels. The pH was fixed at 2.0 due to the characteristics of the raw effluent. Alkaline pH was tested in preliminary experiments and the results were not satisfactory. The experiments were conducted in 100 mL glass flasks, using an incubator shaker operating at 100 rpm and 30 °C for 20 min (determined as equilibrium time in the preliminary tests).

**Evaluation of relative point of zero charge pH (pHPZC*)**

The relative point of zero charge (pHPZC*), i.e. the pH that imparts null electrical charge density on the absorbent particle surface in relation to the effluent, was studied by immersing 1% orange albedo (Madsorbent Veffluent⁻¹) into the effluent diluted to 60% (Veffluent VH₂O⁻¹). The pH was varied from 1.9 to 12.2 using 20% H₂SO₄ and 40% NaOH solutions, totaling 11 trials with distinct pH values. The pHPZC* was obtained by the interception in the pHinitial vs. pHfinal curve, following procedures described in literature but with some modifications (Montanher et al. 2007; Silva et al. 2012). All trials were conducted at 30 °C under stirring of 100 rpm and contact time of 20 min. Color removal was also performed over evaluation of pHPZC*.

**Factorial experimental design**

The experiments were conducted according to a 2³ full factorial design with three replicates at the central point, totaling 11 experimental conditions, with % Effluent (20 to 100%), orange albedo concentration (0.5 to 2.5%), and pH (2.0 to 9.0) as the variables and their respective levels. The study of different pH values, even after determining the orange albedo pHPZC* had the purpose of examining the pH effect on the other variables. The % Effluent (Equation (4)) was defined as the percentage of textile wastewater used for diluting a given volume of bidistilled water.

\[
\%\text{Effluent} = \frac{V_{\text{wastewater}}}{V_{\text{wastewater}} + V_{\text{waste}}} \times 100 \text{ (Dilution)}
\]

where a dilution rate of 100% corresponds to the raw effluent.

Response surface methodology was applied on the statistically significant variables and analysis of variance (ANOVA) was used to validate the regression model (Equation (5)).

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_i X_i^2
\]

where Y is the model response, β₀ is a constant, and βᵢ, βᵢⱼ are the linear, quadratic and interaction coefficients, respectively. All calculations were performed using the Statistica® software.

**RESULTS AND DISCUSSION**

**Characterization of orange albedo**

The orange albedo tested as a biosorbent in this work was dried at 50 °C for 30 h. It can be noticed from its drying kinetics a good fit with the linear model (Moisture Content (%) = -2.4401.Time (hours) + 99.275), with $R^2 = 0.9912$ and around 30 h of drying. Table 1 summarizes the wavenumbers and related functional groups of orange albedo obtained from FTIR.

The range between 1,300 and 909 cm⁻¹ comprises the intermediate region of the FTIR spectrum, with a complex interpretation, as it corresponds to many modes of coupled vibrations. The range 4,000–1,300 cm⁻¹ comprises the typical absorptions of important functional groups, such as -OH, -NH, -C=O, among others. The spectrum indicates the presence of vibration bands of aromatic groups between 1,610 and 1,310 cm⁻¹. It could be observed that the most significant functional groups belong to fibers and carbohydrates, which are typically found in this kind of citrus residue (Table 1). Previous reports have pointed out that these functional groups favor adsorptive processes (Montanher et al. 2007; Boniolo et al. 2010).

A visual and spectroscopic examination of albedo powder (Figure 1) indicated a rough surface. Optical microscopy
observations suggested that the 30 mesh-milled residue was comprised of porous and finely segregated particles, with heterogeneous and uneven surfaces. According to Weber et al. (2013), such features may favor the diffusion and adsorption of dye molecules into the internal space of the biomass.

Physico-chemical characterization of orange albedo is presented in Table 2. The albedo exhibited a large carbohydrate content (Ca), which is ascribed to its insoluble (lignin and cellulose) and soluble (pectin and hemicellulose) portions.

**Characterization of raw textile effluent**

The raw textile effluent supplied by a cotton dyeing factory presented a blue color. According to the supplier’s information, this effluent was collected at the end stage of the dyeing plant, thereby having already been diluted with washing and finishing waters. Table 3 shows that this raw textile effluent contains a very high total solids content. A fraction of approximately 35% of solids corresponded to fixed mineral residue, metals specifically, which may compete with dye molecules for the binding sites of the biosorbent, as well as hamper the biosorbent. In the UV-Vis analyses, the effluent presented only a single absorbance peak centered at 672 nm during and after the adsorption tests.

Textile effluents usually display total solid content and COD values in the range 1,000–1,600 mg L\(^{-1}\) and 200–600 mg L\(^{-1}\), respectively (Braile & Cavalcante 1979). Across the several treatment and finishing stages, COD values tend to oscillate between 20 and 5,200 mg L\(^{-1}\), while the pH varies from 6 to 14 (EPA 1978).

### Table 1  Main FTIR vibration bands of orange albedo

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Spectral range</th>
<th>Description</th>
<th>Probable compounds*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,273.20</td>
<td>3,000–3,500</td>
<td>Stretching vibration of hydroxyl groups (OH)</td>
<td>Water, cellulose and phenols</td>
</tr>
<tr>
<td>1,361.74</td>
<td>1,328–1,464</td>
<td>Angular deformation in plane of CH</td>
<td>Lignin and carbohydrates (as hemicellulose)</td>
</tr>
<tr>
<td>1,625.99</td>
<td>1,508–1,651</td>
<td>Symmetric stretching of C = C or C = O</td>
<td>Lignin</td>
</tr>
<tr>
<td>2,918.29</td>
<td>2,900–2,940</td>
<td>Symmetric stretching (\text{CH}_2)</td>
<td>–</td>
</tr>
<tr>
<td>1,008.77</td>
<td>1,000–1,100</td>
<td>Vibrations of C–O–C and C–O bonds from polysaccharides alcohol</td>
<td>–</td>
</tr>
</tbody>
</table>

*Pastore et al. (2008).
Table 2 | Physico-chemical characterization of orange albedo and other wastes

<table>
<thead>
<tr>
<th>Reference</th>
<th>%F</th>
<th>%U</th>
<th>%C</th>
<th>%P</th>
<th>%L</th>
<th>%Ca</th>
<th>%PEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>12.23 ± 2.95</td>
<td>10.05 ± 0.10</td>
<td>3.46 ± 0.07</td>
<td>3.38 ± 0.09</td>
<td>1.74 ± 0.28</td>
<td>69.14</td>
<td>8.04 ± 0.55</td>
</tr>
<tr>
<td>Tozatti et al. (2013)</td>
<td>9.52</td>
<td>–</td>
<td>–</td>
<td>5.12</td>
<td>8.47</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Clemente et al. (2012)</td>
<td>7.17 ± 0.47</td>
<td>0.96 ± 0.06</td>
<td>–</td>
<td>11.08 ± 0.40</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Montanher et al. (2007)</td>
<td>–</td>
<td>8.60 ± 0.10</td>
<td>3.17 ± 0.01</td>
<td>7.30 ± 0.40</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Santos et al. (2010)</td>
<td>39.15 ± 0.78</td>
<td>7.18 ± 0.15</td>
<td>3.88 ± 0.07</td>
<td>3.72 ± 0.28</td>
<td>0</td>
<td>46.07</td>
<td>–</td>
</tr>
</tbody>
</table>

average ± standard deviation.

Table 3 | Characterization of raw textile effluent from a cotton dyeing company

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (average ± standard deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.71</td>
</tr>
<tr>
<td>COD (mg O₂ L⁻¹)</td>
<td>2,250 ± 473</td>
</tr>
<tr>
<td>Total solids content (mg L⁻¹)</td>
<td>3,410 ± 43</td>
</tr>
<tr>
<td>Fixed total solids content (mg L⁻¹)</td>
<td>1,267 ± 95</td>
</tr>
<tr>
<td>Fixed mineral residue (mg L⁻¹)</td>
<td>1,170 ± 104</td>
</tr>
<tr>
<td>λ_max (nm)</td>
<td>672 ± 2</td>
</tr>
</tbody>
</table>

Preliminary batch trials

In order to evaluate the adsorptive potential of the orange albedo, an analytical calibration curve was prepared from effluent solutions of various known concentrations (Abs = 0.0051.%Effluent + 0.0105, R² = 0.9963). The raw effluent was used in the first experiments, and the results were expressed as color removal percentages (Figure 2). It was noticed that only a slight dye adsorption (color removal of 7.8–15%) occurred when the effluent was used in its raw state. This can be explained by the fact that the raw effluent does not contain only dye (10–15%), but also surfactants and other complex organic substances (Ueda et al. 2004). All these compounds can interfere on the dye adsorption process by inactivating the albedo binding sites, or even by destroying its organic structure.

In parallel, it was noticed that COD increased over time, reaching a maximum value at 20 min. This was possibly due to the organic composition of the orange albedo. The results shown in Table 3 revealed a large quantity of carbohydrates in the albedo, but only a minor fraction of these carbohydrates was found to be insoluble fibers (cellulose + lignin). Hence, most of the fibrous albedo structure is composed of soluble fibers which could be easily solubilized in contact with the alkaline raw effluent. This could explain the increases of COD shown in Figure 3, and suggests that the textile effluent must be diluted in order to prevent the orange albedo from chemical degradation.

Evaluation of effluent dilution and biomass concentration in acidic pH

The experiments carried out on the raw effluent at pH 2.0 resulted in better performances in comparison with preliminary results (alkaline solution). The biomass concentration of 1% was considered to be adequate, which reached 82% of color removal and better efficiency biomass (82% of color removal % biomass⁻¹) (Figure 3(a)). However, the COD removal was not satisfactory, and probably another factor is important.

The shortcomings of pH and biomass concentration were partially solved and the color removal was improved. Experiments using diluted effluent were performed to evaluate the color and COD removal (Figure 3(b)). The performance using 60% of effluent reached around 84% of COD removal (and 82% of color removal), showing that the dilution rate is an important factor on the biosorption process. This behavior can be explained by the dilution of inhibiting compounds such as salts, surfactants, and heavy metals (Sud et al. 2008; Salleh et al. 2011). Textile effluents are generally treated by...
biological oxidation which is not an efficient approach for removing color and dyes from wastewater (Kunz et al. 2002; Cunico et al. 2009). If adsorption process is successful in eliminating dyes from effluents, and the remaining liquid has larger COD, the effluent could be submitted to a biological degradation. However, in addition to the dye, the effluent could present non-biodegradable contents, which need to be evaluated if the use of biological treatment is desired. More studies must be conducted on effluents and modifications of biosorbent structures in such way that the adsorbent degradation could be avoided (Montanher et al. 2007; Ngah & Hanafiah 2008).

Reactive dyes, likewise named azo dyes, account for approximately 60 to 70% of the total amount of dyes used in the textile industry for colouring polyester and cotton fibers, and their residues can be harmful to any living organism (Cunico et al. 2009; Li et al. 2016). Table 4 lists some azo dyes, their specific light absorption wavelength and optimal pH range in which the highest dye removal efficiency has been achieved. The characteristic blue colour of the effluent used in this work was caused by the presence of an anionic reactive dye. This was presumed due to the effluent source, and the adsorption behavior (pH and \(\lambda_{\text{max}}\)) of the albedo/effluent pair obtained from the preliminary adsorption trials.

### Evaluation of relative point of zero charge pH (pH\(_{\text{PZC}}^*\))

With basis on the above mentioned results, the raw effluent was diluted to 60% \(V_{\text{effluent}}/V_{\text{total}}\), and the adsorption process was examined for several pH values (1.9 to 12.2) in order to delimit the pH range at which color is highly removed. Both dilution and pH adjustment procedures did not alter the light absorption range of the blue dye \(\lambda_{\text{max}} = 672\) nm. Data reported in Figure 4 indicated that the albedo was efficient in adsorbing the blue dye from the diluted effluent, with highest color removal of approximately 80% at pH ≤ 2.27. The orange albedo had a pH\(_{\text{PZC}}^*\) of 4.61 (Figure 4). Similar pH\(_{\text{PZC}}^*\) values have been observed for orange albedo with the same grain size, for instance, pH\(_{\text{PZC}} = 4.25\) (Montanher et al. 2007). Surface pH values of 4.44 and 4.38 have also been reported in other studies (Clemente et al. 2012; Tozatti et al. 2013).

The adsorption process of anionic dyes is favored under pH < pH\(_{\text{PZC}}^*\) because of the protonation of functional groups exposed at the albedo surface, and consequent establishment of electrostatic interactions with the anionic dye molecule (Svirasta et al. 2008). It is worth mentioning that the effluent dilution was a crucial step to assess these pH effects.

### Table 4 | Anionic reactive dyes, bio-adsorbent and optimal pH range for dye adsorption

<table>
<thead>
<tr>
<th>Dye</th>
<th>Adsorbent</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>Optimal pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive black 5 (RB5)</td>
<td>Activated carbon</td>
<td>599</td>
<td>&lt;5</td>
<td>Cunico et al. (2009)</td>
</tr>
<tr>
<td>Blue 2</td>
<td>Chitosan</td>
<td>619</td>
<td>&lt;2</td>
<td>Kimura et al. (1999)</td>
</tr>
<tr>
<td>Black 5</td>
<td>Chitosan</td>
<td>599</td>
<td>&lt;2</td>
<td>Kimura et al. (1999)</td>
</tr>
<tr>
<td>Blue 5G</td>
<td>Activated carbon</td>
<td>610</td>
<td>&lt;2</td>
<td>Schimmel et al. (2010)</td>
</tr>
<tr>
<td>Turquoise QG</td>
<td>Activated carbon</td>
<td>668</td>
<td>&lt;2</td>
<td>Schimmel et al. (2010)</td>
</tr>
<tr>
<td>Remazol blue</td>
<td>Buriti stipe</td>
<td>595</td>
<td>1</td>
<td>Silva et al. (2012)</td>
</tr>
<tr>
<td>Blue 5G</td>
<td>Orange albedo</td>
<td>610</td>
<td>&lt;4</td>
<td>Stroher et al. (2012)</td>
</tr>
</tbody>
</table>
Several equations were studied in order to describe the adsorption process. However, the best fitting was obtained with Equation (6), which corresponds to a non-linear correlation whose constants have physical connotations, as illustrated in Figure 4. The first term ($A_{\text{MAX}}$) represents the maximum dye removal rate while the second term represents the decrease of color removal rate provoked by the pH increase.

\[
\% \text{Color Removal} = A_{\text{MAX}} - \frac{(A_{\text{MAX}} - A_{\text{MIN}})}{(1 + 10^{\left[pH_{\text{MAX}} - pH \right]b})},
\]

where $A_{\text{MAX}}$ and $A_{\text{MIN}}$ are the maximum and minimum color removal percentages (%), respectively; $pH_{\text{MAX}}$ is the pH value from which there is a strong decrease in the dye removal rate, i.e. $pH_{\text{MAX}}$ is the critical pH; and $b$ is a constant.

It was clearly observed that the color removal percentage markedly decreased from 90% to 10% when the pH was increased. Such behavior denotes the anionic nature of the blue dye. By analysing the model’s constants, it can be seen that the critical pH value is 2.59 from which the color removal decreased significantly. This was expected since the albedo pHZC* was 4.61, and adsorption of anionic dyes is favored at lower pH values. Equation (7) illustrates the constants of the model to Equation (6), where the correlation had a standard error of 9.7% and $R^2 = 0.9686$.

\[
\% \text{Color Removal} = 89.73 - \frac{(79.45)}{(1 + 10^{\left[pH - 2.59 \times 3.07 \right]})},
\]

Experimental design

A full $2^3$ factorial planning with three repetitions at the center point was performed in order to best fit the model. The results obtained, as well as the details of each experiment, are summarized in Figure 5. It is seen that similar responses were obtained in relation to color removal and COD, meaning that the examined variables have influence on the adsorption process. The negative response values suggest an increase in the variables probably due to the albedo degradation in some trial conditions. This could possibly have influenced the light absorption and COD, consequently increasing both parameters (Stroher et al. 2012).

In terms of color removal, the most significant variables are in descending order, where pH > effluent dilution > biomass concentration. The pH played an antagonist role, i.e. the higher the effluent pH the lower the color removal (Figure 5(a), 5(c), 5(e) and 5(g)). This fact was expected from the previous experiments involving the effluent pH. The biomass concentration also exhibited antagonist influence on the adsorption process, mostly because of the albedo degradation, which affected not only the COD but also the light absorption and pH at equilibrium (Figure 5(e)–5(h)).

The pH is the most important factor in dye adsorption processes, driving not only the adsorption capacity of the adsorbent, but also the solution color and dye solubility (Aksu 2005). pH also determines the magnitude of electrostatic charges that are transferred by the ionized dye molecules (Salleh et al. 2011) and, therefore, their interaction with the adsorbent surface.
Industrial textile effluents also contain salts, heavy metals and surfactants, which can interact with the adsorbent, leading to changes that may diminish recovery of the adsorbent and its efficiency, and process outputs (Aksu 2005).

The dilution rate also significantly influenced the COD removal (Figure 5(a), 5(b), 5(e) and 5(f)). It was found that the lower the dilution rate the higher the COD removal. A datum previously mentioned was the large total solid content of the raw effluent, and the presence of other compounds which compete with the dye for the albedo binding sites. The effluent dilution had the purpose of diminishing these interferences, making the surface binding sites accessible to interact with the blue dye molecule.

Thus, the high adsorption efficiency (80–90%) reached in this study denotes the potential of orange albedo as a...
biosorbent for treatment of diluted textile effluent, considering that such high efficiency could not be reached if the treatment were performed on the raw effluent (Silva et al. 2012).

The treatment process was fitted adequately in the regression model. This was seen by the coefficient ($R^2$) values of 0.9588 and 0.9777 for color removal and COD, respectively (Pareto’s graphics, surface responses and ANOVA table are shown as Supplementary Files – Figure S1 and Table S1, available with the online version of this paper).

Additional comments: considerations on scaled-up operation

The main variables that influence the adsorption process using biomass are temperature, pH, substances concentration, presence of interfering compounds, and biomass concentration (Aksu 2005). The temperature was held constant at 30 °C due to the average climate conditions of the region, thus minimizing heating or cooling costs. The pH and biomass concentration were optimized in the present study, whereas the concentrations of substances and interfering compounds corresponded to the COD determinations, which were simple but revealed the actual contamination level of the textile effluent.

The amount and number of interfering compounds, in addition to the dye, are large, and the specificity would be very important only if a biological treatment, rather than an adsorption process, is applied. This is because microorganisms could be susceptible to toxicity.

Regarding the discharge of effluents into water bodies, the Brazilian legislation (CONAMA Resolution No. 357/2005 and 430/2011 – National Environmental Council, Brazil) states that wastewaters must present reduced chemical and biological oxygen demands, and be analyzed with respect to other parameters, for example, the levels of sulfate, ammonia and metals. However, the treated effluent could be reused in the same washing process because of the high adsorption efficiency attained with the orange albedo. This was the original goal of the present work, once the textile industry consumes large water volumes in its processes. A pilot scale must be tested and the interfering compounds quantified to check the possibility of discharging the treated effluent into water bodies or the need for additional simple treatments (if the parameters required by law have not been reached) as a second step before discharging the treated effluent.

In this work, a simple treatment method was proposed as an attempt to recycle the water used in the textile washing process. The method was based on analysis such as COD (quantification of organic matter among others), color (representing the dye under correct pH) and total solids (indication of salinity of the effluent).

It is known that pH adjustment and effluent dilution would represent the main challenges to scale up the adsorption process. This is because a pH equal to 2 needs to be reached in order to maximize the color removal from the effluent, which is a feature of anionic reactive dyes. The effluent presents a very high pH (~11). The most commonly used methods for pH lowering is the addition of strong acids or carbon dioxide.

The pH adjustment using strong acids (hydrochloric, sulfuric or nitric acids) is generally reported (Arica & Baynamoglu 2007; Wang et al. 2008; Hameed 2009), not only due to the adjustment rapidity, but also due to the small acid volumes needed to reach the desired pH, although the precision is hindered by the sensibility of the variable to strong acids.

The use of carbon dioxide for regulating pH has many advantages, including safe storage, more accurate adjustment, neutralization without secondary effects (addition of substances to the effluent) and low corrosion. However, the use of CO$_2$ only can result in pH values as low as 6 due to the equilibrium of carbon species in aqueous medium, which is ideal for biological processes or processes involving cationic dyes (methylene blue) (Wang et al. 2008; Hameed 2009), but not for the case of the present study. CO$_2$ could be used to reduce the amount of acid, by first performing carbonation until pH 6 and then adding acid to reach pH 2.

Concerning the dilution, water saving in industries is a worldwide concern that is listed among the principles of Green Chemistry and process sustainability. Therefore, the original idea was to recycle the water used in the washing process and adsorption process itself. However, high efficiency on the removal of color and COD emphasizes that the effluent treated with orange albedo can be launched into water bodies, either directly or after minor adjustments.

Biodegradation, advanced oxidation, heterogeneous photocatalysis, adsorption and membrane technology are among the main processes used to treat textile effluents (Kunz et al. 2002; Rangabhashiyam et al. 2013). The adsorption process is particularly important due to its simplicity and reduced use of chemical/micro-organisms, with high removal rates, especially when using a low-cost bioadsorbent. For the other processes, it is necessary to implement several steps to reach the metabolic/reactive conditions of degradation and oxidation, in addition to the high cost to
purchase and maintain the membranes, and the high consumption of energy.

**CONCLUSIONS**

The orange albedo powder was effective as a biosorbent for treatment of textile effluent. The color removal and COD reached, respectively, 89% and 84% at pH values lower than 2 for the effluent diluted to 60% (v v~−1~). The optimized dye adsorption condition was determined to be 60% effluent dilution, 1% albedo concentration and pH equal to 2. The color removal was mainly influenced by pH, while the COD removal was affected by dilution rate.

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