Biosorption of anionic textile dyes from aqueous solution by yeast slurry from brewery

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ABSTRACT

This study investigated the biosorption of the anionic textile dyes: Reactive Red 239 (RR239), Reactive Black B (RBB) and Direct Blue 85 (DB85) according to pH, biomass dosage, contact time and dye concentration onto waste beer yeast slurry. The kinetics and isotherm of the removal of dyes were also studied. The equilibrium of biosorption reaction was reached after 30 min for the reactive dyes and after 60 min for the direct dye. Optimum decolorization was observed at pH 2 and 0.63 g/L of biomass dosage. The kinetic data of the three dyes were better described by the pseudo second-order model. The adsorption process followed the Langmuir isotherm model and the biosorption capacity being estimated to be 152.9, 162.7 and 139.2 mg/g for RR239, RBB and DB85, respectively. Our findings indicated that the waste beer yeast slurry was an attractive low-cost biosorbent for the removal of anionic textile dyes from aqueous solution.

Key words: bioadsorptive decolorization, waste beer yeast slurry, biosorption kinetics, biosorption isotherms.

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THE AIM OF THIS STUDY WAS TO INVESTIGATE THE POTENTIAL USABILITY OF WASTE BEER YEAST SLURRY (WBYS) FOR THE DECOLORIZATION OF AQUEOUS SOLUTIONS CONTAINING THE ANIONIC TEXTILE DYES: C.I. REACTIVE RED 239, C.I. REACTIVE BLACK B AND C.I. DIRECT BLUE 85. EFFECTS OF INITIAL pH, CONTACT TIME, DYE AND BIOSORBENT CONCENTRATION WERE EVALUATED. IN ORDER TO OBTAIN A BETTER UNDERSTANDING OF THE BIOSORPTION MECHANISMS FOR FUTURE APPLICATIONS IN REAL SCALE, THE KINETICS AND ISOTHERM OF REMOVAL OF DYES WERE ALSO STUDIED.
MATERIAL AND METHODS

Dyes
Anionic textile dyes, i.e., C.I Reactive Red 239, C.I. Reactive Black B and C.I. Direct Blue 85 were purchased from Têxtil São João (São João da Boa Vista, SP, Brazil), and used as received, without further purification. The chemical structures of the dyes are shown in Table 1. Stock solutions of the dyes were prepared by dissolving the powdered dyestuff in distilled water (1.0-5.0 g/L). The maximum absorbance ($\lambda_{\text{max}}$) of the individual dyes was determined by a UV-Visible spectrophotometer (Hach DR6000).

Table 1 - Structure and characteristics of the anionic textile dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Chemical Structure</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Mw (g/mol)</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive Red 239</td>
<td><img src="image1.png" alt="Chemical Structure" /></td>
<td>542</td>
<td>1136.32</td>
<td>Monoazo</td>
</tr>
<tr>
<td>Reactive Black B</td>
<td><img src="image2.png" alt="Chemical Structure" /></td>
<td>597</td>
<td>991.82</td>
<td>Diazo</td>
</tr>
<tr>
<td>Direct Blue 85</td>
<td><img src="image3.png" alt="Chemical Structure" /></td>
<td>590</td>
<td>1098.93</td>
<td>Triazo</td>
</tr>
</tbody>
</table>

Waste beer yeast slurry (WBYS) purchased from a brewery in Brazil was used as biosorbent material. The WBYS was autoclaved at 121 °C for 40 min to kill the yeast cells and ensure that the removal of dyes is due to bioadsorption rather than to biodegradation. In order to estimate the yeast biomass concentration in the waste slurry, it was removed from the suspension by centrifugation (3600xg, 15 min), washed several times thoroughly with distilled water and measured by gravimetric method, after drying at 80 °C, to a constant weight.
Batch biosorption studies
Experiments were conducted with 150 mL Erlenmeyer flasks containing 50 mL of the aqueous solution of dyes. Flasks were agitated on a rotary shaker at 120 rpm and 30 °C. Because adsorption is directly influenced by physicochemical variables, variables such as different pH (2, 4, 6, 8 and 10, adjusted by the addition of 0.1 M HCl or 0.1 M NaOH solutions), initial dye concentration (100, 150, 200, 250, 300 and 350 mg/L) and biomass dosage (0.63, 1.26, 1.89, 2.51 and 3.12 g biomass/L) were evaluated. At the end of each equilibrium experiment, the biosorbent was removed from the suspension by centrifugation (3600xg, 15 min) and the residual dye in the solution was measured quantitatively by a UV–Vis spectrophotometer (Hach DR6000) at $\lambda_{\text{max}}$ of dyes (Table 1). All biosorption experiments were performed in triplicates and the dye removal efficiency, R (%), and dye biosorption capacity ($q_e$) of biomass at the equilibrium were calculated according to the Equations (1) and (2), respectively:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100$$

$$q_e = \frac{(C_i - C_e)}{B}$$

where $C_i$ and $C_e$ are the initial and the equilibrium dye concentrations (mg/L) and $B$ is the biosorbent concentration in the solution (g/L).

Kinetic studies
In this study, the dynamic experimental data were analyzed by the pseudo-first order model (Lagergren, 1898), pseudo-second order (Ho and Mckay, 1998) and the intraparticle diffusion kinetic models (Weber and Morris, 1963). The linear form of the pseudo-first order equation can be expressed as in Equation (3):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

where $q_e$ and $q_t$ are the amounts of dye adsorbed per biomass (mg/g) at the equilibrium and at the time $t$ (min), respectively, and $K_1$ is the pseudo-first order rate constant (1/min). The values of $K_1$ and the predicted $q_e$ are determined from the plot of log ($q_e - q_t$) against $t$.

The linear form of the pseudo-second order model is represented by Equation (4):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}$$

where $q_e$ and $q_t$ are the amounts of dye adsorbed per biomass (mg/g) at the equilibrium and at the time $t$ (min), respectively, and $K_2$ is the pseudo-second order rate constant (g/(mg min)). By plotting $t/q_t$ versus $t$, the models parameters $K_2$ and $q_e$ can be determined.

The intraparticle diffusion model allows to identify the diffusion mechanisms and can be represented by Equation (5):

$$q_t = K_{id} t^{0.5} + C$$

where $C$ is the intercept and $K_{id}$ is the intraparticle diffusion rate constant (mg/(g min$^{0.5}$)). From the plot of $q_t$ against $t^{0.5}$, the values of $K_{id}$ and $C$ can be obtained. If
the plot crosses the origin \((C = 0)\), the adsorption process is controlled only by intraparticle diffusion.

**Isotherm studies**

Langmuir and Freundlich isotherm models were used to describe the equilibrium sorption data (Langmuir, 1918; Freundlich, 1906). The Langmuir isotherm model assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. The linearized form of the Langmuir is given by Equation (6):

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}
\]

where \(q_e\) (mg/g) is the amount of dye adsorbed by the biomass at the equilibrium, \(C_e\) (mg/L) is the dye concentration in the solution at the equilibrium, \(q_{max}\) (mg/g) is the maximum monolayer adsorption capacity, and \(K_L\) (L/mg) is the Langmuir constant related to the affinity of the binding sites and adsorption energy. The plot of \(C_e/q_e\) versus \(C_e\) is employed to generate the values of \(q_{max}\) and \(K_L\).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous adsorption surface and is given by Equation (7):

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

where \(K_f\) ((mg/g)(mg/L)^{-1/n}) and \(n\) (dimensionless) are Freundlich constant related to the adsorption capacity and adsorption intensity, respectively. \(K_f\) and \(n\) can be evaluated by plotting \(\ln q_e\) and \(\ln C_e\).

**RESULTS AND DISCUSSION**

**Effect of pH**

The initial pH of the solution significantly influences the dye biosorption process because it affects the adsorbate solubility and the ionizing functional groups of the cell walls (Aksu and Dönmez, 2003; Khataee et al., 2013). Figure 1 illustrates the effect of different initial pH on the removal of three dyes at a dye concentration of 100 mg/L for 60 min, 30 °C and 3.12 g biomass/L. At pH 2, it was observed the highest values of biosorption of dyes: 96% (DB85), 99% (RR239) and 100% (RBB). As the pH of the aqueous solution increased, the removal of the three dyes by the biomass decreased. This effect is related to the protonation of functional groups on the surface of the biomass under acidic conditions, resulting in net positive charge on the biomass (Wu et al. 2011). The electrostatic interactions between the positively charged biosorbed and the negatively charged dye anions lead to dye removal from the solution. As the pH of the medium increases, the number of negatively charged sites increases on the biomass surface, which does not favor the adsorption of dye anions due to the electrostatic repulsion (Iscen et al. 2007; Akar et al. 2009). Similar pH trends were reported by other researchers for yeast biomass (Aksu and Dönmez, 2003; Wu et al., 2011; Wang and Guo, 2011).
Fig. 1. Effect of pH on the dye removal efficiency of WBYS (biosorbent dosage = 3.12 g biomass/L, dye concentration = 100 mg/L, contact time = 60 min, temperature = 30 ºC).

**Effect of biosorbent dosage**

Figure 2 shows the effect of biosorbent dosage (0.63, 1.26, 1.89, 2.51 and 3.12 g/L) on the biosorption of dyes. As can be seen, the percentage of removal increased when the biomass dosage improved. The biosorption capacity, however, decreased from 117.7 to 30.5 mg/g for DB85, from 119.7 to 29.4 mg/g for RR239 and from 130.6 to 29.3 mg/L for RBB when the biomass dosage increased from 0.63 to 3.12 g/L. The decrease in the biosorption capacity at higher WBYS dosage can be attributed to the adsorption sites that remained unsaturated during the adsorption reaction, whereas the number of sites available for adsorption is increased by increasing the biosorbent dosage (Zou et al., 2006). Another reason may be due the interaction of particles such as the aggregation, leading to a decline in the total biosorbent surface area. This fact causes a decrease in the amount of dye biosorbed per unit of weight of biomass (Shukla et al., 2002; Crini and Badot, 2008). Whereas the greatest biosorption capacity was observed at 0.63 g/L, this biosorbent dosage was used in subsequent studies.

![Fig. 2. Effect of biosorbent dosage on the dye removal efficiency of WBYS (dye concentration = 100 mg/L, contact time = 60 min, pH = 2, temperature = 30 ºC).](image)

**Effect of contact time**

Contact time is one important parameter for the successful deployment of biosorbents for practical application. The ideal biosorption materials should be
capable of quickly adsorbing high concentrations of dyes from the wastewater and establishing the equilibrium (Iscen et al., 2007, Khataee et al., 2013). The influence of the contact time on the biosorption capacity of the WBYS for three dyes can be seen in Figure 3. Results showed that a rapid biosorption of dyes occurred at 5 min and reached 59% (DB85), 65% (RR239) and 76% (RBB), respectively. After the first 5 min, the biosorption of dyes were gradually slowed down until the equilibrium, which was achieved at 30 min for RR239 and RBB and at 60 min for DB85. The rapid biosorption of the three dyes by the WBYS in the first 5 min can be attributed to the high availability of active sites on the cell surface. As these functional groups are gradually occupied, the biosorption became less efficient.

**Effect of initial concentration of dye**

The initial concentration of dye provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and the solid phases (Aksu and Dönmez, 2003). In this study, dye removal capacity of the WYBS was investigated using solutions of dyes that ranged from 50 to 350 mg/L, with pH 2 and temperature of 30 °C. The dye removal efficiency and the biosorption capacity of the WBYS are given in Figure 4. Despite the decrease in dye removal efficiency with the increase in the initial dye concentration, the biosorption capacity was increased. The biosorption capacity reached maximum values of 139.0 and 160.8 mg/g for DB85 and RR239, respectively at 250 mg/L and 158.7 mg/g for RBB at 300 mg/L. Dye removal efficiency was higher at lower initial dye concentration because all dye concentration may interact with the binding sites on the cell surface while at higher dye concentration, the binding sites on the biomass surface are saturated and no further biosorption occurs. A decrease in the biosorption capacity observed at RR239 concentration above 250 mg/L can be related to the repulsive forces between the dye molecules at the adjacent sites on the cell surface, which leads to a removal of some dye molecules from the surface (Iscen et al., 2007).
Biosorption kinetics

Kinetics studies are important for designing and optimizing the biosorption system. In this study, kinetic studies of dyes removal were conducted using 150 mL Erlenmeyer flasks with 50 mL of dye aqueous solution (100 mg/L), 0.63 g biomass/L, at various contact times (5-60 min), at 30 ºC and 120 rpm. The parameters calculated for the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models are listed in Table 2. Although the pseudo-first order model has generated a good fit ($R^2 > 0.96$ for all dyes, Fig. 5), the experimental $q_e$ values (119.7, 130.6, 120.1 mg/g for RR239, RBB, and DB85, respectively) did not agree with those that were calculated ($q_1$) (Table 2). On the other hand, the pseudo-second order model generated the best fit ($R^2 > 0.99$ for all dyes, Fig. 6) and the biosorption capacities ($q_2$) estimated by the models were also close to those acquired by the experiments. In the case of intraparticle diffusion model, the correlation coefficients were between 0.83 and 0.98 and the C values were different from zero indicating that the intraparticle diffusion is not the only rate-limiting step (Fig. 7). These results suggest that the biosorption of dye by the WBYS is complex and may involve more than one mechanism. The biosorption process was probably controlled by a chemisorption reaction, but a thermodynamic evaluation is necessary to confirmation this process. The chemisorption reaction involves the sharing or exchanging of electrons between biomass and dye until the surface active sites were fully occupied. Once the activated sites of the external surface reached saturation, the dye molecule diffused into the biomass network was adsorbed onto the active sites in the interior of the biosorbent particle (Malik, 2004; WU et al., 2011).
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Fig. 5 Pseudo first-order kinetic plots for the anionic dyes removal efficiency of the WBYS.

Fig. 6 Pseudo second-order kinetic plots for the anionic dyes removal efficiency of the WBYS.

Fig. 7 Intraparticle diffusion kinetic plots for the anionic dyes removal efficiency of the WBYS.
Table 2 - Kinetic parameters estimated by the pseudo first-order, pseudo second-order and intraparticle diffusion models for the RR239, RBB and DB85 biosorptions on the WBYS.

<table>
<thead>
<tr>
<th>Model</th>
<th>Pseudo-first order</th>
<th></th>
<th></th>
<th>Pseudo-second order</th>
<th></th>
<th></th>
<th>Intraparticle diffusion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$ (1/min)</td>
<td>$q_1$ (mg/g)</td>
<td>$R^2$</td>
<td>$K_2$ (g/(mg min))</td>
<td>$q_2$ (mg/g)</td>
<td>$R^2$</td>
<td>$K_{id}$ (mg/(g min$^{0.5}$))</td>
<td>$C$ (mg/g)</td>
</tr>
<tr>
<td>RR239</td>
<td>0.0615</td>
<td>15.62</td>
<td>0.968</td>
<td>0.0093</td>
<td>121.23</td>
<td>1.000</td>
<td>2.3411</td>
<td>103.38</td>
</tr>
<tr>
<td>RBB</td>
<td>0.0612</td>
<td>10.34</td>
<td>0.993</td>
<td>0.0145</td>
<td>131.53</td>
<td>1.000</td>
<td>1.4410</td>
<td>120.35</td>
</tr>
<tr>
<td>DB85</td>
<td>0.0527</td>
<td>31.05</td>
<td>0.995</td>
<td>0.0037</td>
<td>123.49</td>
<td>0.999</td>
<td>4.1651</td>
<td>89.26</td>
</tr>
</tbody>
</table>

**Biosorption isotherm**

The equilibrium biosorption isotherm is prerequisite to understand how adsorbates interact with adsorbents and how they could be used for design purpose. In this study, $q_e$ as a function of the dye concentration at the equilibrium plot was fit with the Langmuir and Freundlich isotherm equations. Table 3 lists the Langmuir and Freundlich adsorption isotherms constant with the correlation coefficients. It could be seen that the Langmuir isotherm fits better ($R^2>0.99$ for all dyes, Fig. 8) than the Freundlich isotherm (Fig. 9). These results revealed that the biosorption process was based on the monolayer adsorption. The maximum biosorption capacities ($q_{max}$) calculated by the Langmuir model were 152.93, 162.73 and 139.16 mg/g for RR239, RBB and DB85, respectively.

**Fig. 8** Langmuir isotherms for the biosorption of RR239, RBB and DB85 on the WBYS.

**Fig. 9** Freundlich isotherms for the biosorption of RR239, RBB and DB85 on the WBYS.
The essential features of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter, $R_L$ (Mckay et al., 1982):

$$R_L = \frac{1}{1 + K_L C_i}$$

where $C_i$ is the highest initial dye concentration (mg/L). $R_L$ can be used for the interpretation of the adsorption process as follows: irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The $R_L$ values found were 0.011, 0.009 and 0.023 for DB85, RR239 and RRB respectively, indicating that the sorption process is favorable.

**Table 3 - Biosorption isotherm constants for RRB239, RBB and DB85 biosorptions on the WBYS.**

<table>
<thead>
<tr>
<th>Model</th>
<th>$q_{max}$ (mg/g)</th>
<th>$K_L$ (L/mg)</th>
<th>$R^2$</th>
<th>$K_F$ (mg/g)</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR239</td>
<td>152.93</td>
<td>0.310</td>
<td>0.992</td>
<td>86.59</td>
<td>9.12</td>
<td>0.668</td>
</tr>
<tr>
<td>RBB</td>
<td>162.73</td>
<td>0.123</td>
<td>0.998</td>
<td>104.14</td>
<td>13.14</td>
<td>0.918</td>
</tr>
<tr>
<td>DB85</td>
<td>139.16</td>
<td>0.265</td>
<td>0.999</td>
<td>99.57</td>
<td>16.50</td>
<td>0.865</td>
</tr>
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</table>

**CONCLUSION**

The present study revealed that waste beer yeast slurry can be used as biosorbent to remove three anionic textile dyes (RRB239, RBB, DB85) from aqueous solution. The biosorption process of dyes proved to be dependent on the pH of the solution, on the contact time, biosorbent dosage and initial concentration of dyes. Optimum pH and biosorbent dosage were determined as being 2.0 and 0.63 g/L, respectively. Batch studies showed that the kinetics were well described by the pseudo-second-order model, and the equilibrium was well described by the Langmuir model. In conclusion, waste beer yeast slurry may be an economic, effective and eco-friendly option for the removal of anionic dyes from aqueous media.

**ACKNOWLEDGMENTS**

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