ADMI color removal from biological treated textile effluent using powdered activated carbon

Remoção de cor ADMI de efluente têxtil após o tratamento biológico utilizando carvão ativado em pó

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Abstract

Textile mill effluents have a complex composition and even after biological treatment, they still contain high concentrations of dyes and pigments. Activated carbon adsorption has been widely studied for dye removal; however, most studies use synthetic wastewater instead of real textile mill effluent. The objective of this study was to evaluate the efficiency of color and COD removal from a real textile mill effluent using powdered activated carbon (PAC). The iodine number was measured to characterize the PAC used. The textile effluent color was measured be the ADMI method. The maximum removal efficiency reached was 60% for COD, and 93% for color, using 20 g. L⁻¹ of adsorbent. Furthermore, with a PAC concentration of 4 g. L⁻¹, it was possible to reach the legal color limit for Minas Gerais, Brazil. The results proved the feasibility of using PAC for color and COD removal from real textile industry.

Keywords: Adsorption. Activated Carbon. Textile Effluent. ADMI Color and COD Removal.

Resumo

Efluentes de fábrica têxtil têm composição complexa e, mesmo após o tratamento biológico, ainda apresentam elevada concentração de corantes e pigmentos. A adsorção em carvão ativado tem sido extensivamente investigada para a remoção de corantes, porém a maioria dos trabalhos utilizam efluentes sintéticos ao invés de efluente têxtil real. O objetivo deste trabalho foi avaliar a eficiência de remoção de cor e DQO de um efluente têxtil real com a adsorção em carvão ativado em pó (PAC). Para a caracterização do PAC, foi medido o número de iodo. A cor do efluente foi medida pelo método de cor ADMI. A máxima eficiência de remoção alcançada foi de 60% para DQO e 93% para cor, com 20 g. L⁻¹ de PAC. Ainda, com uma concentração de adsorvente de 4 g. L⁻¹, pode-se alcançar o limite de cor estabelecido pela legislação de Minas Gerais, Brasil. Os resultados mostraram a viabilidade do uso de PAC para remoção de cor e DQO de efluente têxteis.


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Introduction

The textile sector in Brazil plays an important role in the country’s economy, being responsible for 1.7 million jobs, representing 5.5% of the transformation sector income (ABIT, 2013). Coupled with the high number of textile mills in the country, there is a high water demand in this sector, that generates from 0.08 to 0.15 m³ of wastewater per kg of fabric produced (MOUSSA, 2008). Textile mill effluent is a complex mixture of chemical substances that is characterized by high values of color, temperature, pH, chemical oxygen demand (COD), and low biodegradability (JADHAV et al., 2015).

The desizing step, in which sizing materials are removed after the weaving process, is the main source of organic contaminants. On the other hand, the dyeing step is responsible for the greatest effluent volumes. In addition, this step is the source of organic dyes and pigments used to color the textiles (DOS SANTOS; CERVESTES; VAN LIER, 2007). It is estimated that about 10% to 15% of applied dyes are lost to effluents, due to the low dye fixing rate on the textiles (AKERDI et al., 2016).

Esthetic problems in surface waters that receive this type of effluent are evident, even if the effluents have low dye and pigment concentrations (REGTI et al., 2017). More importantly, these substances can block natural light penetration, disturbing the aquatic ecosystem. Toxicity can also arise due to interactions of aquatic organisms with dyes or compounds formed during their degradation (ALJEBOREE; ALSHIRIFI; ALKAIM, 2017). Conventional activated sludge treatment systems are efficient in COD and suspended solids removal for textile effluents, but due to the low biodegradability of dyes and pigments, the removal of these substances is very low (KIM et al., 2004; REGTI et al., 2017). Therefore, even after biological treatment textile effluents need additional processing for recalcitrant compounds removal (ARCANJO et al., 2018).

Conventional tertiary treatment systems, such as coagulation followed by flotation or sedimentation are efficient for particulate matter, but not for color or dissolved organic compounds removal. Activated carbon has been shown to be an efficient material for color removal, since it has a high surface area, and, therefore, a high adsorption capacity (KANCHI et al., 2017).

A variety of studies have shown high activated carbon dye adsorption capacity. Belaid et al. (2013) found high levels of removal of the textile dyes acid blue 113, basic red 5, and relative yellow 81 using commercial activated carbon. Sathishkumar et al. (2012) tested activated carbon produced from the agroindustrial waste Jatropha curcas pods for Remazol Brilliant Blue R removal. Faria et al. (2004) used cationic and anionic dyes to evaluate the efficiency of activated carbon with different chemical surfaces. Methylene blue has been used as model compound to evaluate the efficiency of a variety types of activated carbon for color removal (EL QADA; ALLEN; WALKER, 2006; HAMEED; DIN; AHMAD, 2007; HAMEED; AHMAD; LATIFF, 2007; KAVITHA; NAMASIVAYAM, 2007; KUMAR; JENA, 2016; TAN; AHMAD; HAMEED, 2008). Although it is important to assess the efficiency of activated carbon for dye removal, there is still a lack of studies using real textile effluents, which are much more complex and difficult to treat.

For highly colored effluents, such as textile wastewaters, that are a mixture of dyes with different absorbance intensities and whose colors differ from the brownish orange cobalt platinum standard, the American Dye Manufacture Index (ADMI) color index is recommended to evaluate treatment efficiency (DE JAGER; SHELTON; EDWARDS, 2014). In addition, ADMI color is the truest measure of water color, regardless of its hue. Thus, it allows for a more accurate quantification of water and wastewater colors (KAO et al., 2001).

Therefore, the aim of this study was to evaluate COD and ADMI color removal of a real textile effluent collected after an activated sludge treatment system, using commercial powered activated carbon (PAC).

Materials and methods

Textile effluent and powdered active carbon (PAC)

The effluent was collected after the secondary settling tank of a conventional activated sludge system of a textile mill, located in Minas Gerais State, Brazil, and stored at 4°C until further analysis. Physicochemical characterization (COD, pH, conductivity, turbidity and ADMI color) was performed according to the Standard Methods for Examination of Water and Wastewater (APHA, 2012). Color was quantified using the ADMI tristimulus filter method, based on absorbance at three different wavelengths (438, 540 and 590 nm), with one unit of ADMI color equivalent to 1 mg L⁻¹ PtCo.

PAC was purchased from Alphatec, with granulometry of 4 μm. For PAC characterization, the iodine number was determined according to the Brazilian standard method NBR 12073 MB 3410 (ABNT, 1991a).
Adsorption test

To determine the PAC adsorption capacity, suspensions of 0.0g, 0.2g, 0.4g, 0.6g, 0.8g, 1.0g and 2.0g of PAC in 50 mL of effluent were prepared. These suspensions were maintained under constant agitation of 80 r pm for 24 h at 22°C, in duplicate. Following, the samples were filtered on qualitative filter paper (28 µm) for PAC removal before color, COD and pH analysis. Color and COD removal efficiencies (RE) were calculated according to equation (1) and the amount adsorbed per unit mass adsorbent (qe) was calculated according to equation (2):

\[ RE(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \]  
\[ q_e = \frac{(C_0 - C_e) \cdot V}{m} \]

where \(C_0\) and \(C_e\) represent the initial and equilibrium values of ADMI color or COD, respectively; \(q_e\) is the equilibrium adsorption capacity (mg.g\(^{-1}\)); \(V\) represents the solution volume in liters; and \(m\), the PAC mass used in grams.

The results were fitted to the Freundlich (equation 3), and Langmuir (equation 4) models using SigmaPlot 11.0 software.

\[ q = K_f C_e^{1/n} \]  
\[ q = \frac{q_0 b C_e}{1 + b C_e} \]

where \(K_f\) is the Freundlich constant (mg.g\(^{-1}\),(mg.L\(^{-1}\))\(^{1/n}\)); \(n\) is the adsorption intensity constant; \(q_0\) is the maximum coverage capacity of the monolayer (mg.g\(^{-1}\)); and \(b = \) Langmuir constant (L.mg\(^{-1}\)).

Results and discussions

Textile effluent characterization

Physicochemical parameters of the textile effluent and the maximum permissible limits established in Minas Gerais state legislation for effluent discharge to receiving waters (Joint Normative Deliberation COPAM/CERH n°01/2008) are presented in Table 1.

COD, pH and turbidity values were within the normative values. However, effluent color was more than three-fold the legal limit because of the high load of dyes in the textile production process that produced highly colored effluent that the activated sludge biological treatment process could not remove, thereby making tertiary treatment such as adsorption necessary.

Iodine number

The PAC used had an iodine number of 947 mg g\(^{-1}\) that is above the lower limit recommended in Brazilian (ABNT, 1991b) and North American (AWWA, 1991) standards of at least 600 mg.g\(^{-1}\) and 500 mg.g\(^{-1}\), respectively. For comparison, iodine numbers for commercial PAC used to treat textile effluents are presented in Table 2. The iodine number for the PAC used in this work was considered high compared to those used by Kadirvelu et al. (2000) and Coelho, Vazzoler and Leal (2012), and similar to those used by Al-Degs et al. (2000) and Bestani et al. (2008). The relatively high iodine number indicated that the PAC had a high number of micropores and a large surface area, since the adsorption of 1 mg of iodine corresponds to 1 m\(^2\) of internal surface of the activated carbon (EL-HENDAWY; SAMRA; GIRGS, 2001).

Table 2: Iodine numbers for activated carbons found in literature

<table>
<thead>
<tr>
<th>Iodine number (mg.g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>425</td>
<td>(KADIRVELU et al., 2000)</td>
</tr>
<tr>
<td>530</td>
<td>(COELHO; VAZZOLER; LEAL, 2012)</td>
</tr>
<tr>
<td>947</td>
<td>This study</td>
</tr>
<tr>
<td>950</td>
<td>(BESTANI et al., 2008)</td>
</tr>
<tr>
<td>1050</td>
<td>(AL-DEGS et al., 2000)</td>
</tr>
</tbody>
</table>

Source: The Authors.

Table 1: Physicochemical characterization of textile effluent and legal discharge limits

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Results</th>
<th>Legislation limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>143 (ADMI)</td>
<td>75 mg.L(^{-1}) PtCo</td>
</tr>
<tr>
<td>COD</td>
<td>78 mg.L(^{-1})</td>
<td>250 mg.L(^{-1})</td>
</tr>
<tr>
<td>Turbidity</td>
<td>3 NTU</td>
<td>100 NTU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1745 µS.cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>8.5</td>
<td>6 – 9</td>
</tr>
</tbody>
</table>

Source: The Authors.
Adsorption test

COD and ADMI color removal

COD and ADMI color removals as a function of PAC concentration are presented in Figure 1. Removal efficiencies increased with the PAC concentration up to 20 g. L\(^{-1}\) of adsorbent, reaching 60% for COD and 93% for color. Above this PAC dose, removal efficiencies remained relatively constant. This may be explained by some organic compounds having low affinity to the PAC used or by reaching the maximum adsorption capacity of the PAC for ADMI color and COD. In any case, to meet the Minas Gerais state discharge limit, a dose of 4 g. L\(^{-1}\) was sufficient, resulting in remaining color of 74 (ADMI).

Figure 1: COD and ADMI color efficiency removal after adsorption with active carbon at pH 8.5 and 22 °C over 24 h.

Fonte: The Authors.

The removal efficiency reached in this work was high compared to other studies that also tested PAC for textile effluents (Table 3). It is important to highlight the differences among the color measurement methodologies used by each author, making comparison a difficult task. The only study found in which color was measured at three wavelengths was that of Pala and Tokat (2002), who used PAC in the aeration tank of an activated sludge system at a lower concentration than used in this study and reached a somewhat lower removal efficiency of 86%. All other studies measured color removal at only one wavelength, which is not recommended since textile effluents contain a mixture of dyes that present maximum absorbance at different wavelengths. Furthermore, in all the studies except two (SIRIANUNTAPIBOON, SANSAK; SIRIANUNTAPIBOON, SADAHIRO, SALEE, 2007), color removal was higher than COD removal, probably because other compounds besides dyes had lower affinity for the adsorbent and they remained in solution contributing to effluent COD after the adsorption process. The 24-hour reaction time was higher than used in some studies listed in Table 3, but since no kinetic study was undertaken, it is possible that the time necessary to reach adsorption-desorption equilibrium could be much lower.

Adsorption isotherms

Adsorption isotherms are presented in Figure 2 and adsorption constants in Table 4 for textile effluent COD and ADMI color removals. COD results adjusted better to the Freundlich isotherm, whereas for ADMI color, the Langmuir isotherm was a better fit (higher \(R^2\)). The Freundlich model is usually more suitable for complex mixtures than the Langmuir model, since the former is an empirical model that describes the sorption of solutes on a solid (FYTIANOS; VOUDRIAS; KOKKALIS, 2000).

Parameters \(q_o\) of the Langmuir equation and \(K_f\) of the Freundlich equation are used to estimate the maximum adsorption capacity for various chemical compounds (SODRÉ, LENZI and COSTA, 2001), whereas parameter b of the Langmuir equation relates to the distribution of the compound in the liquid phase and on the surface of the adsorbent (VIANA, 2013) and the parameter n of the Freundlich equation is used to qualitatively verify the adsorption intensity, indicating the affinity of the adsorbent to the component to be adsorbed.

ADMI color adsorption fitted better to the Langmuir model and the relatively low value of the Langmuir adsorption constant (b) indicates that desorption rate was lower than adsorption rate (VIANA, 2013). COD fitted better, although poorly, to the Freundlich model, for which the adsorption capacity (n) was less than 1 (Table 4), indicating that the adsorption process was unfavorable and that there were no highly energetic sites on the surface of the material. The very low \(K_f\) value indicates that the PAC had a low adsorbate retention capacity (MULLER et al., 2009). Despite the unfavorable COD response, effluent COD was already in accordance with legislation before the adsorption process and the COD removal achieved was due to removal of dyes, as shown in Figure 1.

For the Langmuir model, the maximum adsorption capacities for COD and ADMI color removals were extremely high, especially when compared to Ahmad and Hammed (2009), who found values of 29,154 and 24,396 mg.g\(^{-1}\) for color (455 nm) and COD, respectively, using an activated carbon produced from bamboo residues for the treatment of a textile wastewater.
Table 3: Maximum COD and color removal efficiencies (RE) for textile effluent using activated carbon reported in the literature

<table>
<thead>
<tr>
<th>Adsorbent type</th>
<th>COD RE(%)</th>
<th>Color Measure method</th>
<th>Adsorbent concentration (g.L⁻¹)</th>
<th>Contact time</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial PAC</td>
<td>60</td>
<td>ADMI</td>
<td>20</td>
<td>24h</td>
<td>8.5</td>
<td>This study</td>
</tr>
<tr>
<td>Sawdust from coconut palm PAC</td>
<td>56</td>
<td>Abs 540nm</td>
<td>30</td>
<td>1h</td>
<td>9.7</td>
<td>(KADIRVELU et al., 2000)</td>
</tr>
<tr>
<td>PAC added to a activated sludge system</td>
<td>78</td>
<td>Abs 445nm; Abs 540nm; Abs 660nm</td>
<td>0.4</td>
<td>HRT = 1.6d; θc = 30d</td>
<td>7 – 7.5</td>
<td>(PALA; TOKAT, 2002)</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>64</td>
<td>Abs 535nm</td>
<td>7.5</td>
<td>7.5d</td>
<td>NI</td>
<td>(SIRIANUNT APIBOON; SADAHIRO; SALEE, 2007)</td>
</tr>
<tr>
<td>Activated carbon produced from coconut coal</td>
<td>85</td>
<td>Abs 550nm</td>
<td>7.5</td>
<td>7.5d</td>
<td>NI</td>
<td>(SIRIANUNT APIBOON; SANSAK, 2008)</td>
</tr>
<tr>
<td>Activated carbon produced from bamboo residues</td>
<td>75</td>
<td>Abs 455nm</td>
<td>3</td>
<td>10h</td>
<td>3</td>
<td>(AHMAD; HAMEED, 2009)</td>
</tr>
<tr>
<td>Activated carbon produced from bamboo residues</td>
<td>74</td>
<td>Abs 465nm</td>
<td>3</td>
<td>NI</td>
<td>NI</td>
<td>(AHMAD; HAMEED, 2010)</td>
</tr>
</tbody>
</table>

*NI = Not Informed; HRT = Hydraulic Retention Time; θc = Solid Retention Time.

Source: The Author.

Figure 2: Adsorption for (a) COD removal and (b) ADMI color removal of textile effluent.

Source: The Authors.

pH after adsorption

The pH increased slightly with the increase in PAC concentration. For 16g.L⁻¹ of adsorbent, the pH reached 9.1, which was higher than the legal limit. Using the minimum concentration of PAC to reach the color limit (4g.L⁻¹), the pH was 9, which was just within the Minas Gerais State limit of 6 to 9.
Table 4: Isotherm model parameters for the adsorption of textile effluent

<table>
<thead>
<tr>
<th></th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>COD</td>
<td>0.0003</td>
<td>0.3854</td>
</tr>
<tr>
<td>ADMI color</td>
<td>46.4111</td>
<td>1.7313</td>
</tr>
</tbody>
</table>

$K_f$ = Freundlich experimental constant (mg g$^{-1}$(mg L$^{-1}$)$^{1/n}$); $n$ = adsorption intensity experimental constant; $q_0$ = maximum coverage capacity of the monolayer (mg g$^{-1}$); $b$ = Langmuir constant (L mg$^{-1}$).

Source: The Author.

Conclusion

The iodine number of the tested PAC was significantly higher than the value established in Brazilian standards and was within the range of values found in the literature. COD and color removals from real textile effluent were high compared to those reported in previous studies. With only 4 g L$^{-1}$ of PAC, it was already possible to reach the color discharge limit for Minas Gerais State. Therefore, tertiary treatment of textile effluent using PAC for color removal is a feasible process.

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References


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