Use of submerged anaerobic membrane bioreactor (SAMBR) containing powdered activated carbon (PAC) for the treatment of textile effluents

B. E. L. Baêta, R. L. Ramos, D. R. S. Lima and S. F. Aquino

ABSTRACT

This work investigated the use of submerged anaerobic membrane bioreactors (SAMBRs) in the presence and absence of powdered activated carbon (PAC) for the treatment of genuine textile wastewater. The reactors were operated at 35°C with an HRT of 24 h and the textile effluent was diluted (1:10) with nutrient solution containing yeast extract as the source of the redox mediation riboflavin. The results showed that although both SAMBRs exhibited an excellent performance, the presence of PAC inside SAMBR-1 enhanced reactor stability and removal efficiency of chemical oxygen demand (COD), volatile fatty acids (VFA), turbidity and color. The median removal efficiencies of COD and color in SAMBR-1 were 90 and 94% respectively; whereas for SAMBR-2 (without PAC) these values were 79 and 86%, In addition, the median values of turbidity and VFA were 8 NTU and 8 mg/L for SAMBR-1 and 14 NTU and 26 mg/L for SAMBR-2, indicating that the presence of PAC inside SAMBR-1 led to the production of an anaerobic effluent of high quality regarding such parameters.

INTRODUCTION

Wastewater from textile industries is normally generated in the steps of destarching, mercerization, dying and washing (Kumar et al. 2008) and contains significant amounts of organic compounds such as dyes. These compounds provide high color to the effluent.

It is estimated that about 15% of dyes produced worldwide are lost to the environment due to their incomplete fixation during the step of fiber dyeing. Some dyes and/or their degradation byproducts might be carcinogenic and have mutagenic properties, especially those containing the azo-aromatic function as a chromophore.

Textile effluents can be treated by a variety of processes, which include biological and physical–chemical schemes. In Brazil most textile industries employ, for treatment of their wastewater, the well known biological process of activated sludge. Such a process is normally efficient in removing the organic load from wastewater, but is not so effective in decolorizing it. The use of activated carbon or coagulants might be used as a complement, but normally generates a high amount of sludge that needs to be properly handled (Santos et al. 2009). According to some researchers (van der Zee et al. 2003; van der Zee & Villaverde 2005), currently there is no single technology capable of efficiently and economically removing color from textile effluents, which keeps open research opportunities in this field.

One technology that has the potential of being used for color removal of textile effluents is anaerobic digestion (Georgiou et al. 2004). In anaerobic conditions, textile pollutants such as the azo dyes (which represent around 70% of the dyes produced worldwide) can be used as electron acceptors, leading to the reduction of the azo bond (–N=–N–) and production of amines, mostly aromatic. Indeed, different research groups have demonstrated that removal efficiencies varying from 60 to 80% can be obtained during the anaerobic treatment of azo dye solutions (Méndez-Paz et al. 2005; Dos Santos et al. 2006).

The upflow anaerobic sludge blanket reactor (UASB) has been widely applied in Brazil for the anaerobic treatment of different industrial wastewater (Ex. dairy, slaughterhouse, food processing) due to its inherent advantages, such as the ability of allowing a high sludge age.

Key words | activated carbon, anaerobic decolorization, redox mediator, submerged anaerobic membrane bioreactor (SAMBR), textile effluent

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without the need of sludge granulation, as well as the low degree of mechanization and energy requirement. In spite of this, there are a handful of papers on the use of UASB reactors for treating textile effluents. For instance, Somasiri et al. (2008) used an UASB reactor hydraulic retention time (HRT) (HRT $= 24$ h) for treating a textile effluent chemical oxygen demand (COD) (COD $= 2,000$ mg/L) and showed that a significant color removal (92%) could be achieved. The authors also observed that toxic byproducts accumulated in the reactor, contributing to reducing overall organic matter removal efficiency.

The low growth of anaerobic microorganisms is the major drawback for the treatment of recalcitrant and toxic effluents, which might be worsened by electron transfer limitations between different species of the anaerobic consortia and by hydraulic shocks. One strategy to avoid the washout of anaerobic microorganisms from UASB reactors would be the use of microfiltration membranes which could be submerged in the digestion compartment or in the upper part of the reactor (settler compartment). In its turn, one way of improving electron transfer between species and enhancing the kinetics of microbial growth is to add redox mediators to the anaerobic system.

According to Dos Santos et al. (2005) the use of redox mediators increases the efficiency of color removal during anaerobic treatment of textile effluents as such compounds are reduced by the reducing equivalents produced by microbial cells (e.g. NADH, FADH) which are then re-oxidized by the azo dye, thereby enhancing the decolorization kinetics. Indeed, different authors have demonstrated that compounds such as riboflavin (vitamin B2) and sulfonated antroquinones (AQS) can act as redox mediators (Cervantes et al. 2001; Rau et al. 2002; Field & Brady 2003).

As the degradation of azo dyes in anaerobic systems leads to the formation of aromatic amines that can be toxic to microorganisms, one strategy to control any impairment of the anaerobic consortia is to use activated carbon inside the bioreactor. Besides minimizing toxicity, the activated carbon would also help in controlling membrane fouling due to the adsorption of proteins and other biopolymers, as demonstrated by Akram & Stuckey (2008b).

Therefore, the main objective of this paper is to present results on the anaerobic degradation of textile effluent in a bench scale submerged anaerobic membrane bioreactor (SAMBR) in the presence of powdered activated carbon (PAC) and yeast extract as source of redox mediator.

**MATERIALS AND METHODS**

**Experimental apparatus and operational conditions**

Two SAMBRs were built using polyvinyl chloride (PVC) pipes and joints, and each reactor had a working volume of $3.25$ L. The microfiltration membranes ($0.8$ m$^2$ of hollow fiber, with nominal pore size of $0.4$ μm) were made of polyimide and the module was manufactured by PAM membranes (PAM – Membranas Seletivas®). The modules were placed inside the settler compartments of the SAMBR, as shown in Figure 1.

SAMBR-1 was operated with $4.0$ g L$^{-1}$ of PAC in its interior, whereas SAMBR-2 was the control reactor and operated without PAC. Both reactors were operated at $35$ C using an HRT of $\sim 24$ h. During operation the pH was kept in the range of 6.8–7.2 by adding Na$\text{$_2$}$CO$_3$ 0.1 mol L$^{-1}$ or HCl 0.01 mol L$^{-1}$ directly into the reactor, despite the fact that the yeast extract solution contained sodium bicarbonate as buffer and micro- and macronutrients. The concentration of these compounds varied and was determined for each textile effluent in order to maintain a minimum COD:N:P proportion of 350:5:1 as suggested by Chernicharo (2007).

The SAMBR were incubated with $0.8$ L$^{-1}$ of anaerobic sludge ($10$ g L$^{-1}$) from a demo scale UASB reactor fed with raw sewage in operation at the Centre for Research and Training on Sanitation (CePTS) UFMG/COPASA, located at the Arrudas WWTP, which receives the major part of the domestic sewage of the urban area of Belo Horizonte city (Minas Gerais state, Brazil).

Both reactors were fed for 90 days with textile wastewater diluted 10 times with the yeast extract solution which provided alkalinity, micronutrients and the redox mediator riboflavin ($50$ μg/g yeast extract). The industrial effluent was collected in the equalization tank of a textile industry (Itabirito, MG, Brazil) for six times along the operation period, as shown in Table 1. The collected effluent was kept under stir in a fridge ($5$ C) during the SAMBR feeding in order to minimize microbial growth and significant changes in the effluent characteristics.

**Analytical procedures**

During the SAMBR operation, samples of influent and effluent were collected five times a week for the analyses of chemical oxygen demand (COD), color, pH and turbidity. In addition, samples of anaerobic effluents and from inside the SAMBR were collected once a week for analysis of

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*References*

- Akram & Stuckey (2008b)
- Cervantes et al. (2001)
- Field & Brady (2003)
- Dos Santos et al. (2005)
- Field & Brady (2003)
- Chernicharo (2007)
- Somasiri et al. (2008)
volatile fatty acids (VFA). COD, pH and turbidity analyses followed the procedures detailed in the Standard Methods for the Examination of Water and Wastewater (APHA 2005).

COD analysis was carried out in the supernatant obtained after centrifuging the sample at 5,000 rpm for 15 min (Fanem Excelsa 11 centrifuge, Model 206 BL), hence COD results refer to the soluble fraction. For color analysis, it was used a Dell colorimeter previously calibrated with Pt/Co standards, hence the results are given in color units (CU) which are equivalent to Hazen units.

VFA analyses were carried out by high performance liquid chromatography (HPLC) using an Aminex HPX-874 (BioRad) which was kept at 55°C under isocratic mode (0.6 ml min⁻¹ of H₂SO₄ 0.01 mol L⁻¹). For this, 10 μL of the centrifuged samples was injected in a Shimadzu equipment so that the separated VFA could be detected at 210 nm in a diode array detector (DAD). The VFA method was properly validated as detailed elsewhere (Mesquita et al. 2011).

VFA concentrations were then used to estimate the fraction of COD due to such intermediate compounds of the anaerobic digestion, according to Equation (1).

\[
\text{COD}_{VFA} = 0.35 \times [\text{formate}] + 1.07 \times [\text{acetate}] + 1.51 \\
\times [\text{propionate}] + 1.82 \times [\text{butyrate} + \text{isobutyrate}] \\
+ 2.04 \times [\text{valerate} + \text{isovalerate}]
\]  

(1)

Table 1 | Characteristics of the textile effluent used to feed the SAMBR

<table>
<thead>
<tr>
<th>Effluent sampling</th>
<th>Total solids (mg/L)</th>
<th>Suspended solids (mg/L)</th>
<th>Turbidity (NTU)</th>
<th>Color (CU)</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>Kjeldahl nitrogen (mg/L)</th>
<th>Time of operation (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>1,213</td>
<td>524</td>
<td>191</td>
<td>29,200</td>
<td>8.8</td>
<td>730</td>
<td>9.8</td>
<td>1–15</td>
</tr>
<tr>
<td>2nd</td>
<td>1,024</td>
<td>237</td>
<td>118</td>
<td>36,500</td>
<td>9.2</td>
<td>1,100</td>
<td>18.1</td>
<td>16–30</td>
</tr>
<tr>
<td>3rd</td>
<td>1,206</td>
<td>446</td>
<td>99</td>
<td>24,800</td>
<td>8.9</td>
<td>873</td>
<td>14.9</td>
<td>31–45</td>
</tr>
<tr>
<td>4th</td>
<td>902</td>
<td>343</td>
<td>102</td>
<td>30,280</td>
<td>10.1</td>
<td>797</td>
<td>11.5</td>
<td>46–60</td>
</tr>
<tr>
<td>5th</td>
<td>1,389</td>
<td>645</td>
<td>167</td>
<td>28,900</td>
<td>8.7</td>
<td>971</td>
<td>15.2</td>
<td>61–75</td>
</tr>
<tr>
<td>6th</td>
<td>1,233</td>
<td>505</td>
<td>132</td>
<td>30,657</td>
<td>8.5</td>
<td>927</td>
<td>14.7</td>
<td>76–90</td>
</tr>
<tr>
<td>Average value</td>
<td>1,161</td>
<td>450</td>
<td>135</td>
<td>30,056</td>
<td>9.0</td>
<td>900</td>
<td>14.0</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 1 | COD changes in the influent and effluent of SAMBR-1 (with PAC) and SAMBR-2 (control, without PAC).
Critical flux estimate

In order to evaluate the effect of PAC on the membrane permeability, the permeate flow rate was measured as a function of the flux through the membrane in both SAMBRs. Such experiments lasted 32 days and the SAMBRs were fed industrial wastewater in order to maintain the following theoretical membrane fluxes: 1.8; 3.6; 7.2 and 14.4 L m\(^{-2}\) h\(^{-1}\) (LMH). The reactors were then operated at each condition for 8 days after which the membranes were withdrawn for chemical cleaning before starting the next condition. The effluent flow rate was measured three times a day and the critical condition was verified when there was a significant difference between the influent and permeates flow rates.

Statistical analysis

In order to verify whether the differences observed between the SAMBR were statistically significant, statistical tests were employed by means of the software Statistica\(^{®}\). The Shapiro–Wilk test was used to confirm that the results did not follow normal distribution, and then non-parametric tests (Kruskal–Wallis ANOVA, Student–Newman and Mann–Whitney) were applied. A p-value lower than 0.05 was adopted for rejecting the null hypothesis (\(H_0\)).

RESULTS AND DISCUSSION

Figure 2(a) shows the changes in COD removal efficiency in both SAMBRs as the time of operation went by. The median COD removal in SAMBR-1 (with PAC) was 90% whereas in SAMBR-2 (control, without PAC) it was 79%, and such a difference was statistically significant (p-value <0.05). The median COD removal efficiency observed in SAMBR-1 (90%) was relatively high when compared with the results presented by Akram & Stuckey (2008a) who measured efficiencies as high as 97% when a SAMBR was fed with an easily biodegradable carbon source (sucrose) in the presence of PAC (1.67 g L\(^{-1}\)) employing an HRT of 20 h.

The median influent COD was 605 and 615 (mg/L) for SAMBR-1 and SAMBR-2, respectively, whereas in the effluent these values were 59 and 128 (mg/L), respectively. These results imply that the presence of PAC inside the SAMBR-1 led to an improved effluent quality, probably because it helped biomass adaptation and boosted microbial activity. One hypothesis is that PAC adsorbed toxic organics, such as aromatic amines formed from anaerobic reduction of the azo-dyes present in the textile effluent, thereby minimizing microbial inhibition and enhancing COD removal. In addition, PAC might also have adsorbed soluble recalcitrant compounds (e.g. dyes, surfactants) thereby increasing their retention time and leading to a higher removal of soluble COD. Adsorption of organics onto PAC might allow the formation of an attached biofilm which can then degrade the adsorbed organics, thereby freeing adsorption sites.

Figure 2 also shows that no trend in reduction of COD and color removal efficiencies was observed throughout the reactors’ operation (90 days). For SAMBR-1 (with PAC) the COD removal efficiency remained pretty stable
along the operation, indicating that saturation of PAC adsorption sites was not reached. This implies that adsorption could not solely account for COD removal, and suggests that some adsorbed organics (e.g. dyes, aromatic amines and VFA) are metabolized by anaerobic microorganisms, thereby freeing PAC adsorption sites. It is not known whether microorganisms can uptake adsorbed molecules directly from the PAC surface or whether such molecules are desorbed as their concentrations are reduced in the bulk phase following their metabolization.

Regarding the color removal, Figure 2 shows that there was little difference between SAMBR-1 and SAMBR-2 performances. The conditions for microbial growth and COD removal in SAMBR-2 were not as good as those observed in SAMBR-1, nevertheless the color removal remained high and followed the SAMBR-1 pattern. This finding might indicate that azo dye degradation and color removal do not depend on the development of specialized microorganisms as suggested by Baeta et al. (2011).

Another explanation for the higher COD removal in the SAMBR-1 is related to the statistically significant (p-value < 0.05) difference between the CODVFA measured in both SAMBRs. Figure 3 shows that there was a lower amount of VFA inside the SAMBR-1 which might be due to a combination of higher VFA degradation rates associated with the better biomass acclimatization, and some degree of VFA adsorption by the PAC. Lower amounts of VFA in the bulk solution, mainly acetate, would minimize thermodynamic constraints and favor the conversion of propionate and/or butyrate, thereby enhancing the growth of acetogenic microorganisms.

During the SAMBR operation it was observed that the VFA concentration inside the reactors was higher when compared with the effluent (Figure 3), indicating that the passage of the anaerobic effluent through the membrane contributed to reducing the VFA concentration. As it is very unlikely that a microfiltration membrane can retain low molecular weight compounds such as acetate and propionate, one hypothesis to explain the reduction of VFA is the development, at the membrane surface, of a biofilm capable of degrading the passing intermediate compounds.

Regarding color removal, Figure 4(a) shows that both SAMBRs were very efficient, especially when one takes into account the complexity of textile effluent which contains many different dyes belonging to distinct chemical classes. The median removal efficiencies observed in this study (94% for SAMBR-1 and 86% for SAMBR-2) are similar to the values obtained by Cervantes et al. (2000) and Dos Santos et al. (2004) who operated UASB or EGSB reactors, respectively, fed with azo dyes solutions in the presence of anthraquinone 2,6-disulfonate (AQDS) as redox mediator. It is noteworthy that in this work we used yeast extract as a cheap source of the redox mediator riboflavin, and the reactors were operated in the mesophilic range.

Figure 4(a) indicates that the color removal in SAMBR-1 was higher than SAMBR-2 and that true color was less variable in the effluent of SAMBR-1. These results indicate that the presence of PAC inside the SAMBR-1 enhanced color.
removal which might have happened due to a combination of two factors: dye adsorption and dye reduction onto the PAC surface. van der Zee et al. (2003); Mezohegyi et al. (2010) and Pereira et al. (2010) point out that the presence of quinone groups at the PAC surface might act as redox mediators enhancing the azo-dye decolorization kinetics. In this way, reducing equivalents produced by biomass would reduce PAC quinone groups which in their turn would be reoxidized reducing the azo dyes. As the efficiency of color removal from the textile effluent was lower in both SAMBRs in the absence of yeast extract (data not shown) these results indicate that the addition of a soluble source (yeast extract) was more effective than immobilized redox groups present on the PAC surface (FTIR data not shown here). It is important to highlight that the enhanced color removal in SAMBR-1 was not due to simple adsorption, as the PAC was added only at the beginning of the operation and the reactors were run for 90 days. It is likely that the dyes eventually adsorbed were degraded by a reductive mechanism catalyzed by soluble or adsorbed redox mediators, thereby contributing to regeneration of PAC adsorption sites.

One of the main benefits of coupling the microfiltration membrane in the UASB reactor is the control of effluent quality. Figure 4(b) shows that turbidity in the effluent from both reactors was quite low and varied within a narrow range. As time of operation goes by, the nominal membrane porosity is likely to reduce due to fouling, hence it is hypothesized that the microfiltration used retained not only particulate matter, but also colloidal material (proteins, cell lysis products), which is difficult to remove and represents a significant fraction of the soluble COD in UASB effluents (Aquino et al. 2009).

The data shown in Figure 4(b) indicates that the reactor without PAC (SAMBR-2) produced an effluent with higher turbidity values which were more variable. Such a difference was statistically significant (p-value <0.05) and indicates that PAC was efficient in adsorbing colloidal material such as proteins and some soluble microbial products (SMP). Other researchers (Aquino et al. 2006; Akram & Stuckey 2008a) also demonstrated the ability of PAC in retaining high molecular weight compounds, such as proteins, which fall into the colloidal range and cause turbidity, thereby helping in the control of membrane fouling.

Aquino et al. (2006) measured the transmembrane pressure (TMP) in two SAMBRs (3 L) one of which received PAC (1.7 g L$^{-1}$). Both reactors operated continuously under an HRT of 6 h and flux of 20 LMH, and the results showed that while the TMP value was around 25 kPa in the control SAMBR, the pressure averaged 10 kPa in the SAMBR having PAC inside. In another work, Akram & Stuckey (2008b) assessed the effect of PAC on membrane fouling and observed that in the absence of PAC the critical flux was 2 LMH whilst in the presence of PAC (1.7 g/L) this value was 9 LMH.

In the present study we addressed the effect of PAC on membrane permeability and attempted to estimate the critical flux by measuring the influent and permeate flow rates, as shown in Figure 5. It can be seen that in the reactor without PAC (SAMBR-2) the change of flux to values higher or equal to 3.6 LMH resulted in higher head loss and reduction of the measured permeate flow rates. In the reactor with PAC (SAMBR-1), the flux causing a significant head loss and subsequent decrease in permeate flow rate was four times higher (14.4 LMH). This clearly shows the benefits of PAC in improving membrane
fluctuations, which is probably due to the effectiveness of PAC in adsorbing proteins and other colloidal material that causes internal membrane fouling.

**CONCLUSION**

This paper presented results on the operation of SAMBRs, in the presence of yeast extract as a cheap source of the redox mediator riboflavin, for the treatment of real textile effluents. The results showed that the presence of PAC inside SAMBR-1 enhanced reactor stability, membrane permeability (higher critical flux) and performance regarding the removal of COD, VFA, turbidity and color. The median removal efficiencies of COD and color in SAMBR-1 were 90 and 94% respectively; whereas for SAMBR-2 (without PAC) these values were 79 and 86%. PAC adsorbed toxic and intermediate compounds (e.g. aromatic amines and VFA) which enhanced microbial activity and reactor stability, and might also have acted as a source of immobilized redox mediators such as quinone groups. COD, VFA and color removal was not solely due to adsorption as PAC was regenerated in situ by the desorption and/or degradation of the adsorbed compounds. The median permeate values of turbidity and VFA were 8 NTU and 8 mg/L for SAMBR-1 and 14 NTU and 26 mg/L for SAMBR-2, indicating that the coupling of membrane with PAC leads to the production of a high quality effluent which might be reused in the textile industry. The main drawbacks of using PAC inside biological reactors refer to sludge management and increased cost of operation, which must be properly addressed in view of the benefits PAC brings to the SAMBR process.

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