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Bioaugmented membrane bioreactor (MBR) with a GAC-packed zone for high rate textile wastewater treatment

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ABSTRACT

The long-term performance of a bioaugmented membrane bioreactor (MBR) containing a GAC-packed anaerobic zone for treatment of textile wastewater containing structurally different azo dyes was observed. A unique feeding strategy, consistent with the mode of evolution of separate waste streams in textile plants, was adopted to make the best use of the GAC-zone for dye removal. Dye was introduced through the GAC-zone while the rest of the colorless media was simultaneously fed through the aerobic zone. Preliminary experiments confirmed the importance of coupling the GAC-amended anaerobic zone to the aerobic MBR and also evidenced the efficacy of the adopted feeding strategy. Following this, the robustness of the process under gradually increasing dye-loading was tested. The respective average dye concentrations (mg/L) in the sample from GAC-zone and the membrane-permeate under dye-loadings of 0.1 and 1 g/L.d were as follows: GAC-zone (3, 105), permeate (0, 5). TOC concentration in membrane-permeate for the aforementioned loadings were 3 and 54 mg/L, respectively. Stable decoloration along with significant TOC removal during a period of over 7 months under extremely high dye-loadings demonstrated the superiority of the proposed hybrid process.

1. Introduction

Textile wastewater is a complex and highly variable mixture of many polluting substances including dye (Robinson et al., 2001). Azo dyes make up the majority (60–70%) of the dyes applied in textile processing industries (Hunger et al., 2004). Several physicochemical decoloration techniques have been reported in the literature (e.g. adsorption, membrane separation, advanced oxidation process); none, however, has appeared as a panacea due to high cost, low efficiency and limited versatility (Hai et al., 2007). Biodegradation is an environmentally friendly and cost competitive alternative. However, azo dyes are xenobiotic compounds and due to their electron withdrawing nature, they tend to persist under aerobic environment (Knackmuss, 1996). On the other hand, decoloration through reductive cleavage of azo bond (–N=N–) under anaerobic condition has been reported (van der Zee and Villaverde, 2005). The reduction of many azo dyes is, however, a rather slow process (Kapdan et al., 2003; Manu and Chaudhari, 2003; Méndez-Paz et al., 2005).

In different experimental systems, redox mediators such as quinones and flavine-based compounds have been demonstrated to accelerate azo dye reduction by shuttling reducing equivalents from an electron-donating cosubstrate to the azo linkage (Cervantes et al., 2001; Field and Brady, 2003; Rau et al., 2002). Although the redox mediator dosage levels are low, continuous dosing implies continuous expense and continuous discharge of these biologically recalcitrant compounds.

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Therefore, it is desirable to immobilize the redox mediator in the bioreactor. Activated carbon (AC) adsorption has long been used as the polishing decoloration step in the industry (Rozzi et al., 1999). Interestingly it contains surface quinone structures (van der Zee et al., 2002). In view of the simultaneous adsorption and catalytic capacity of activated carbon, biologically activated carbon (BAC) processes have been explored for anaerobic decoloration in a few studies with encouraging results (Mezohegyi et al., 2007; Ong et al., 2008; van der Zee et al., 2002).

It is, however, noteworthy that the formation of highly toxic aromatic amines during anaerobic azo dye decoloration renders a polishing aerobic step a must (van der Zee and Villaverde, 2005; You et al., 2010). The above mentioned studies exploring BAC process address only a part (i.e., decoloration) of the complex issue of textile wastewater management. In this context it is interesting to note that unlike bacterial activated sludge process, aerobic white-rot fungi can degrade wide varieties of recalcitrant compounds including textile dyes (Fu and Viraraghavan, 2001). In fact we previously developed a membrane bioreactor (MBR) implementing a mixed microbial community dominated by white-rot fungi, and demonstrated improved color as well as total organic carbon (TOC) removal as compared to conventional MBR (Hai et al., 2006, 2008b). An MBR was utilized as its several characteristics, such as membrane interception and long sludge retention time, help to prevent washout of the bioaugmented inoculants. We also demonstrated that direct addition of powdered activated carbon (PAC) into the bioaugmented aerobic MBR brings about added advantages including co-adsorption of dye and enzyme onto activated carbon and subsequent enzymatic dye degradation (Hai et al., 2008b). The dye loading rate in that study, however, was rather limited. We envisaged that the integration of an activated carbon-catalyzed anaerobic reactor and aerobic bioaugmented MBR may enable high rate decoloration and TOC removal.

In order to develop a high rate decoloration and TOC removal process, this study explored an innovative MBR with a granular activated carbon (GAC)-packed anaerobic zone beneath the main aerobic zone which contained the membrane module and a mixed microbial community of fungi and bacteria. It was expected that following the primary anaerobic decoloration in the GAC-packed zone, the completion of color and organics removal would be accomplished in the membrane-coupled aerobic zone. Furthermore, a unique wastewater feeding strategy, consistent with the mode of evolution of separate waste streams in textile plants, was adopted in this study. This article reports the effect of such feeding mode and the long-term overall treatment performance of the explored scheme. This is the first report on excellent dye removal performance under very high dye loading with such a membrane-based hybrid process.

2. Materials and methods

2.1. Microorganism and synthetic wastewater

The white-rot fungi *Coriolus versicolor* NBRC 9791 obtained from the NITE Biological Resource Center (NBRC), Japan was used for this study. Although white-rot fungi have been widely reported to excrete a variety of extracellular enzymes under carbon or nitrogen limitation, reports on enzyme secretion under nutrient sufficient condition (Laugero et al., 1996) are also available. It was confirmed that the collected strain was capable of secreting laccase enzyme in nutrient sufficient media (Hai et al., 2008b). Therefore, a nutrient sufficient synthetic wastewater containing dye and starch (2 g/L)—two common components in real textile wastewater—along with urea (0.1 g/L) and other nutrients, was utilized in this study. Details regarding the media have been documented elsewhere (Hai et al., 2008a). For the first 210 days of continuous operation only the azo dye acid orange II was utilized; while for the rest of the operation period all four dyes as listed in Table 1 were fed into the reactor.

2.2. Design and feeding mode of the bioreactor

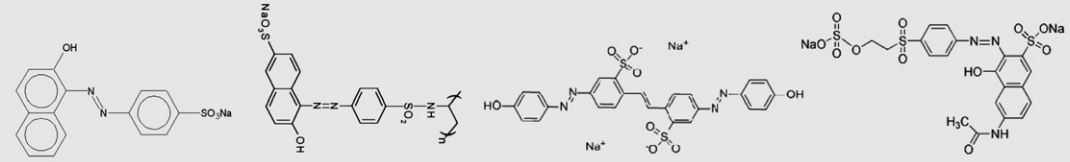
A laboratory-scale, cylindrical PVC reactor (Diameter = 6.7 cm, Height = 24 cm)—with a working volume of 0.85 L and containing a GAC-packed anaerobic zone beneath the main aerobic zone—was operated under a total hydraulic retention time (HRT) of 1 day (Fig. 1). The performance of the MBR was first observed without any GAC-zone. Then the amount of GAC was gradually increased from 0 to 30 g to 60 g and finally to 120 g. The corresponding heights of the aerobic zone were 21, 18 and 12 cm, respectively. GAC F400-OS (average particle size 1.1 mm) received from Calgon Mitsubishi Chemical Corporation, Japan was utilized in this study. The GAC was always washed with Milli-Q water to remove very fine particles and wetted for 24 h before use. In order to avoid the influence of initial dye adsorption, GAC was saturated with dye before addition to the reactor. This was done by pumping through the wetted GAC an amount of dye equivalent to five times the maximum dye adsorption capacity of GAC as estimated by an adsorption isotherm (not shown). Initially, saturated GAC was mixed with partially digested sludge (collected from a long time operated bioaugmented MBR), added into the reactor as slurry and allowed to settle. The aerobic zone, on the other hand, was initially inoculated with pure fungus culture; however, bacterial contamination occurred in absence of any specific means to avoid that, and eventually a stable combined culture of bacteria (40%) and fungi (60%) was obtained in line with a previous study (Hai et al., 2008b). No sludge was withdrawn from the MBRs and no further addition of fresh fungal culture into the MBR was required to maintain fungal dominance. At the time of increasing the amount of GAC in the aerobic zone, the air-diffuser of the reactor was lifted up to allow settling of certain amount of sludge and then a certain amount of GAC was added. The GAC-zone was firm enough not to float and a fairly clear demarcation of the two zones was possible.

Unlike the nutrient-deficient hardly-biodegradable dye bath effluent, different other streams of wastewater in a textile mill, namely, scouring and desizing-effluent, usually contain high concentrations of relatively easily degradable organics. Instead of mixing the different streams originating from a textile plant, efficient use of GAC exclusively for dye adsorption may be made by feeding only the dye effluent through GAC. In our study, all the dye along with a small amount of starch

Table 1 – Outline of the GAC-MBR operation.

Aim	No.	Days	Amount of GAC (g)	Loading through X,Y[a] (g/L.d)				Overall loading[c], (g/L.d)		
				Starch[b]		Dye[b]		Starch	Dye	TOC
				X	Y	X	Y			
A. Effect of GAC-zone	I	14	–	–	2	–	0.1	2	0.1	0.944
	II	7	30							
	III	7	60	0.25	1.75	0.1	0			
	IV	14	120							
B. Effect of feeding mode	I	21	120	2	0	0.1	0	2	0.1	0.944
	II	21		1	1	0.05	0.05			
	III	14		0.25	1.75	0.1	0			
C. Performance under stepwise increased dye loading	I	90	120	0.25	1.75	0.1		2	0.1	0.944
	II	30				0.25			0.25	1.03
	III	30				0.5	0		0.5	1.16
	IV	60				1.0			1.0	1.44
D. Effect of simultaneous feeding of different dyes	I	21	120	0.25	1.75	1	0	2	0.1	1.39

In runs A-C only dye #1 was fed, while all four dyes were fed in run D.



a X : GAC-zone, Y : aerobic zone (see Fig. 1).
b Only starch and dye have been shown as other components were always fed from 'Y', except only when mixed wastewater was introduced through 'X' or simultaneously from 'X', 'Y'(Trial# B-I, B-II).
c Since HRT = 1 day, numerical values of loading and concentration are the same.

(to sustain biological activity in this zone) was fed through the GAC-zone. Same volume of the media—containing rest of the components and representing the effluent from units other than dye bath within a textile plant—was simultaneously fed from the top of the reactor. The overall dye-loading was stepwise increased from 0.1 to 1 g/L.d. Before that, however, the performance of the MBR was observed while feeding the mixed wastewater (containing all the components including dye) through the GAC-zone, or simultaneously through aerobic and GAC-zone, in order to assess the benefit of the feeding strategy explored in this study. The pH of the wastewater was 4.5, while continuous monitoring revealed the maintenance of a pH of 6 ± 0.5 in the bioreactor without any specific control. The experimental plan has been detailed in Table 1. A control MBR with the same design and feeding mode, as in 'C' in Table 1, except that it contained an anaerobic sludge bed devoid of GAC, was operated in order to assess the performance of the anaerobic zone with/without GAC.

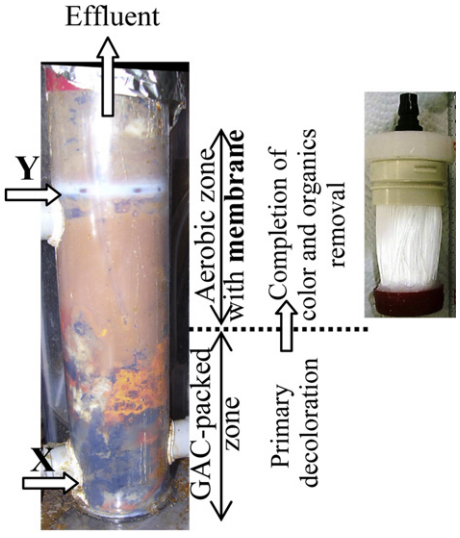


Fig. 1 – Schematic of the bioaugmented MBR with GAC-packed zone (Hydrophilic Polyethylene Hollow fiber module at inset; X, Y: feeding through GAC and aerobic zone, see Table 1 for details).

2.3. *Membrane module*

A 4.5 cm compact bundle (packing density = 56%) of microporous (0.4 μm), hydrophilicaly treated, polyethylene hollow-fibers, obtained from Mitsubishi Rayon, Japan was utilized in this study. As the height of the aerobic zone was gradually reduced, the available 22 cm full-length bundle was cut (and resealed) to fit to that zone. During the final trial, the module had an effective fiber-length and surface area of 5.5 cm and 0.256 cm^2, respectively. Due to the small volume of the reactor and the large surface area of the module, application of only a very low average flux of 0.0033 m^3/m^2.d with a 6 min/50 min (on/off) mode was required. Ex-situ chemical cleaning of the module (backwashing with a NaOCl solution containing

250 mg Cl/L) was applied only once (on day 180) during the whole operation.

2.4. Analytical methods

Samples from a port located just below the top of the GAC-zone were collected to assess the extent of decoloration in the GAC-packed zone, while measurements on membrane-permeate revealed the extent of overall removal. Total organic carbon was measured with a TOC/TN analyzer (TOC-V, Shimadzu, Japan). High performance liquid chromatography (HPLC) using a diode array detector (DAD) was utilized to measure the concentration of dye(s). For the HPLC-DAD analysis, two eluents, acetonitrile and water, in gradient proportions were utilized in conjunction with a Spherisorb ODS2 column (200 by 4.6 mm; 5 μm particles). The corresponding injection volume, flow rate, detection wavelength and column-temperature were 100 μL, 0.8 mL/min, 210 nm and 35 °C, respectively. Membrane-permeate samples were analyzed as collected, while samples collected from within MBR were centrifuged under 2150×*g* to obtain the supernatant and then analyzed for color. The concentration of only the parent compound(s) was monitored. Oxidation-reduction potential (ORP) and dissolved oxygen (DO) were measured to confirm the establishment of anaerobic environment in the GAC-zone. Mixed liquor suspended solids (MLSS) concentration was measured according to the standard methods (Clescerl et al., 2005). The relative abundance of fungi/bacteria in MLSS was monitored by a microscopic and a size-based fractionation method (Hai et al., 2009). Transmembrane pressure (TMP), as an indicator of membrane fouling, was continuously monitored using a vacuum pressure gauge (GC 61, Nagano Keiki Co. Ltd., Japan).

3. Results and discussion

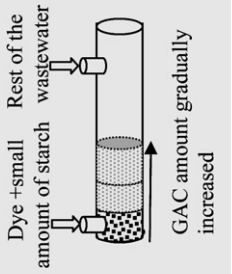
In order to confirm that the color and TOC removal data discussed in this article were obtained under stable operating conditions, periodic monitoring of the stability of the bioaugmented culture in the aerobic MBR and the hydraulic performance of the membrane were performed (data not shown) with the methods outlined in section 2.4. This section will focus on the color and TOC removal performance of the integrated as well as the unit processes.

3.1. Importance of coupling GAC-zone to bioaugmented MBR

When the wastewater with a dye loading of 0.1 g/L.d was fed to the aerobic bioaugmented MBR having no GAC-zone, the dye concentration in the membrane-permeate was 12 mg/L (Table 2). After adding dye-saturated GAC (initial weight 30 g), and passing dye through this zone (while introducing the rest of the media through the aerobic zone) dye in the treated effluent dropped to 1 mg/L only, the corresponding concentration in sample from GAC-zone being 26 mg/L. The dye concentration in the sample from GAC-zone gradually dropped as the amount of GAC was increased (30–120 g). ORP and DO measurements confirmed that due to vigorous aeration in the aerobic zone at the top, anaerobic environment was not completely established in the GAC-zone when the GAC weight was less than 120 g. Our observation confirms that, with the GAC-packed anaerobic zone, an excellent overall decoloration can be achieved in the bioaugmented MBR; however, in order to establish anaerobic environment, a certain height of that zone needs to be maintained.

Table 2 – Effect of GAC-zone on overall dye removal (Dye loading = 0.1 g/L.d).

Amount of GAC, g	Dye concentration after removal (mg/L)	
	After GAC-zone	In permeate
0	–	12
30	26	1
60	8	1
120	3	0



3.2. Effect of adopted feeding mode

Separate wastewater-streams originate from different plants in a textile mill (Hai et al., 2007). If those streams are mixed and fed through GAC, many other compounds, in addition to dye, in that mixed textile effluent can adsorb on GAC (Hai et al., 2007; Hao et al., 1999). To make the best use of the GAC-zone exclusively for dye decoloration, we adopted a unique feeding strategy of passing dye (along with a certain amount of easily degradable organics) through GAC, while simultaneously introducing the rest of the uncolored effluent through the aerobic zone. In order to confirm the efficacy of the proposed feeding strategy, the performance of the MBR was observed under three distinct feeding modes as shown in Fig. 2. The best decoloration both in anaerobic and aerobic zone were obtained with the proposed feeding mode. Reduced anaerobic decoloration was observed when a significant portion or whole of the uncolored fraction of the wastewater along with dye was fed through the GAC-zone. This may be attributed to the competitive adsorption of dye and other compounds on GAC, affecting GAC-catalyzed anaerobic dye degradation. However, a reduced decoloration was also observed in the aerobic zone in this case. This was accompanied by a drop in MLSS concentration in the aerobic zone (Fig. 2). Apparently the substantial adsorption of easily degradable substrate on GAC created an artificial nutrient-deficiency in the aerobic zone, and this led to reduced MLSS concentration and deteriorated aerobic decoloration. The observed effect of MLSS concentration on removal is in line with that of Ren et al. (Ren et al., 2005) who reported low microbial metabolism and consequently low COD removal when the MLSS concentration was below a threshold value of 6 g/L. Furthermore similar effect of substrate deficiency on

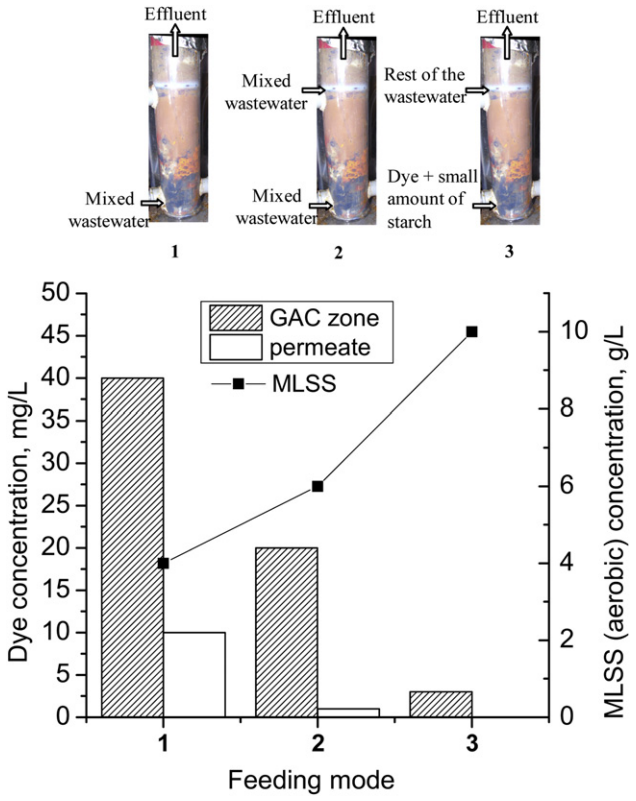


Fig. 2 – Effect of feeding mode on MLSS (aerobic) and dye removal (Dye loading = 0.1 g/L.d).

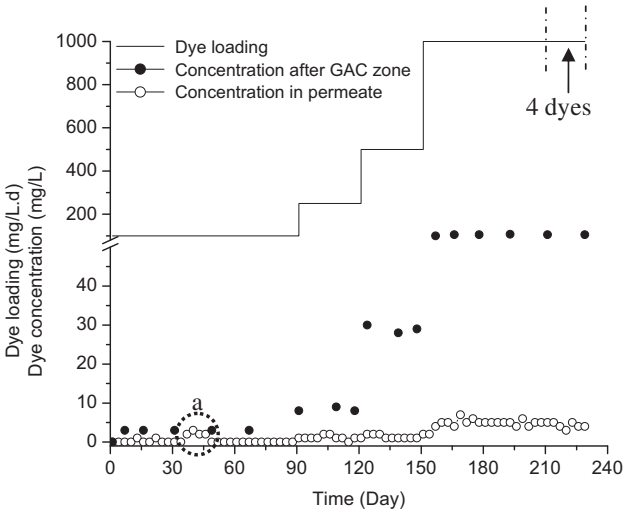


Fig. 3 – Long-term decoloration under gradually increased dye loading (a. temporary deterioration due to air-diffuser malfunctioning).

MLSS concentration and decoloration was reported by Hai et al. (Hai et al., 2008a). Our observations substantiate the efficacy of the adopted feeding strategy as opposed to the conventional practice of completely mixing the dye effluent with the other uncolored streams emanating from a textile mill.

3.3. *Long-term performance under stepwise increased dye-loading*

Although the total HRT utilized in this study was longer than that used in conventional MBRs, a logical way of assessing the reactor performance can be to look at the loading rate. As the dye loading was stepwise increased from 0.1 to 0.25, 0.5 and finally to 1.0 g/L.d, respectively over an operation period of 7 months, the reactor maintained excellent decoloration (Fig. 3). The membrane-permeate was virtually colorless up to the loading of 0.5 g/L.d. Even under the highest loading, the average dye concentration in the membrane-permeate was only 5 mg/L. Van Der Zee et al. (van der Zee et al., 2002) previously demonstrated excellent decoloration of hydrolyzed reactive red 2 under a loading of 0.18 g/L.d in a GAC-packed UASB reactor. Ong et al. (Ong et al., 2008) demonstrated high decoloration of acid orange II under a dye loading of 0.6 g/L.d in a GAC-biofilm sequencing batch reactor. On the other hand, Mezohegy et al. (Mezohegyi et al., 2007) reported excellent decoloration of acid orange II in an up flow AC-packed reactor under a rather high dye loading of 18 g/L.d. However, judging from the very small reactor size (9 mL) and the requirement of continuous bubbling of helium to maintain strict anaerobic condition, the study of Mezohegy et al. (Mezohegyi et al., 2007) appears to be more of a proof-of-concept and the scale-up potential of that system is questionable.

The relative contribution of the anaerobic and aerobic zone to decoloration under various loadings manifested the importance of an integrated process (Table 3). As noted earlier, GAC can perform both adsorption as well as electron shuttling role (essential for anaerobic reduction). The dynamics of adsorption and biodegradation and consequently the dye removal obviously depends on dye loading. The contribution of the bioaugmented aerobic zone to completion of color removal was more convincing under the higher dye-loadings. For instance, when the loading was only 0.1 g/L.d, even the sample from the GAC-zone was almost colorless. Nevertheless, in case of loading of 1 g/L.d, the dye concentration in the sample from the GAC-zone was 105 mg/L. The corresponding dye concentrations in the supernatant of the aerobic zone mixed liquor and membrane-permeate were 16 and 5 mg/L, respectively (Table 3). This observation confirmed that following the initial anaerobic decoloration the bioaugmented culture in the aerobic zone played an important role to improve color removal, and, finally, the membrane contributed to moderate additional removal. Since a microfiltration membrane, which is unable to retain soluble dye by its own, was utilized in this study, the additional dye removal by the membrane can be attributed to the dye retention onto the cake-layer accumulated over the membrane. Such additional removal of dye by membrane in MBR is in line with previous reports (Hai et al., 2009). It is worth-noting here that, in conventional sequential anaerobic–aerobic processes the aerobic stage contributes mainly to organics removal and rarely to decoloration (van der Zee and Villaverde, 2005). However, in our study, which involved a mixed microbial community dominated by fungi, the aerobic stage contributed significantly to decoloration as well. The importance of combining bioaugmented MBR (in contrast to conventional MBR) with GAC-catalyzed anaerobic process lies herein.

Table 3 – Average dye and organics removal in anaerobic and aerobic zone under different loadings of acid orange II dye.

Reactor type	Overall loading (g/L.d)			Concentration after removal (mg/L)			
				After anaerobic zone	In permeate		
	Dye	TOC	TN	Dye	Dye	TOC	TN
MBR with GAC-packed anaerobic zone	0.1	0.94	0.055	3	0	3	2
	0.25	1.03	0.067	8	1	10	2
	0.5	1.16	0.087	30	1	30	10
	1.0	1.44	0.127	105	5[a]	54	21
MBR with sludge-only anaerobic zone	0.25	1.03	0.067	240	96	–	–

a Corresponding dye concentration in aerobic zone supernatant was 16 mg/L.

It is also notable from the data in Table 3 that that the reactor with a GAC-packed anaerobic zone outperformed the one with sludge-only anaerobic zone, confirming the importance of presence of GAC in the anaerobic zone. GAC-packed anaerobic zone and the bioaugmented aerobic zone are therefore essential to form an efficient color removal process.

In addition to dye, textile wastewater contains many other colorless organics. Moreover, it has been reported that aromatic amines arising from anaerobic reduction of azo dyes are very toxic (O'Neill et al., 2000). Although aerobic removal of aromatic amines has been reported in a few studies (Isik and Sponza, 2004), controversies exist (Lourenco et al., 2000). Hence, not only decoloration but also confirmation of removal of TOC is essential. It is noteworthy that in all the above mentioned studies (Mezohegyi et al., 2007; Ong et al., 2008) showing high rate decoloration in AC-packed systems, completion of organics removal under high loading was a special concern. In our study, almost complete removal of TOC and TN was achieved under the lowest (0.1 g/L.d) dye-loading. However, in contrary to the stable decoloration over all the dye-loadings, the total organics removal (especially that of TOC) deteriorated to some extent under the higher dye-loadings (Fig. 4, Table 3). Although the contribution of dye to TOC and TN was rather low for a dye-loading of 0.1, over a 50% increase in overall TOC-loading occurred when the dye-loading was raised to 1 g/L.d (Table 1). Increased loading on the aerobic zone may have caused the observed moderate decline in TOC removal rate. Nevertheless, it should be mentioned that, even under the highest loading, the average TOC and TN in the membrane-permeate was only 54 and 21 mg/L, respectively corresponding to over 96% TOC removal.

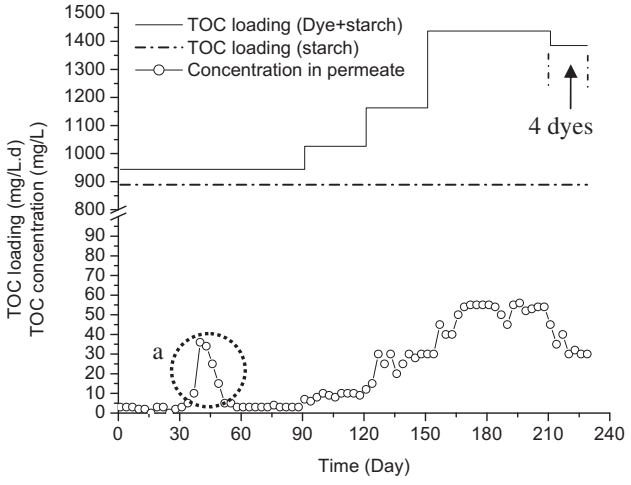


Fig. 4 – Long-term TOC removal under gradually increased dye loading (a. temporary deterioration due to air-diffuser malfunctioning).

3.4. *Performance with structurally different dyes*

The robustness of the developed process was tested by feeding four structurally different dyes (Table 1) in equal loading rates (0.25 g/L.d) resulting in a total dye loading of 1 g/L.d. No deterioration of the decoloration rate was observed during this investigation. Mezohegyi et al. (Mezohegyi et al., 2009) previously tested decoloration of 6 azo dyes in an up flow AC-packed bioreactor; however in that study a single dye was fed during any specific run. Stable decoloration under concomitant high loading of structurally different dyes is, therefore, another unique aspect of the current study.

It is notable that owing to the different carbon contents of the dyes tested, a slight drop in TOC-loading occurred during this period, and this corresponded to a slight improvement in TOC (Fig. 4, from day 210). In fact during an extended observation under a slightly longer HRT a near-complete TOC removal was achieved (data not shown). Stable decoloration along with significant TOC removal over a prolonged period under extremely high dye-loadings evidences the superiority of the proposed hybrid process.

While the current study confirmed the viability of fungi-bacteria bioaugmentation in a lab scale MBR, and the overall hybrid process demonstrated excellent removal performance, issues such as fungal enzyme loss and bacterial disruption of fungal activity may require further special attention in case of real scale application. Related strategies to tackle such shortcomings have been already pointed out in our previous publications (Hai et al., 2008b, 2009) and currently application of such strategies in conjunction with the proposed hybrid process is under investigation.

3.5. *Hydraulic performance of the membrane*

The focus of this study was the removal performance of the proposed hybrid process. Nevertheless it is noteworthy that in addition to the accomplishment of significant color, TOC and TN removal, the membrane fouling in this study was rather minimal. This was manifested by the slight fluctuation of TMP (around 3 kPa) for most part of the operation period (data

not shown). Ex-situ chemical cleaning of the module was applied only once (on day 180) during the whole operation. The fouling avoidance capacity of a spacer-filled, compact module developed on the principle of minimizing intrusion of sludge was demonstrated by Hai et al. (Hai et al., 2008a). Apparently the restricted sway of fibers in the short and rigid module in this study also prevented intrusion of sludge and thereby mitigated fouling. Investigations under realistic higher fluxes are currently ongoing to substantiate the efficacy of short and compact modules.

4. Conclusion

Stable decoloration along with significant organics (TOC, TN) removal over a prolonged period under extremely high dye-loadings was observed in a bioaugmented aerobic MBR with a GAC-packed anaerobic zone. The GAC-packed anaerobic zone played the key role in decoloration, while the aerobic zone was vital for TOC removal. However, in contrast to the limited role of aerobic stage in decoloration in conventional sequential anaerobic–aerobic processes, the aerobic stage in the developed MBR contributed significantly to decoloration under the higher dye-loadings. Our data also evidenced the suitability of a unique wastewater feeding strategy whereby separate streams emanating from a textile plant are selectively split between the GAC-packed and the aerobic zone.

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REFERENCES

Cervantes, F.J., van der Zee, F.P., Lettinga, G., Field, J.A., 2001. Enhanced decolourisation of acid orange 7 in a continuous UASB reactor with quinones as redox mediators. Water Science and Technology 44, 123–128.

Clescerl, L.S., Greenberg, A.E., Eaton, A.D., 2005. Standard methods for examination of water & wastewater 21st ed. American Public Health Association.

Field, J.A., Brady, J., 2003. Riboflavin as a redox mediator accelerating the reduction of the azo dye mordant yellow 10 by anaerobic granular sludge. Water Science and Technology 48, 187–193.

Fu, Y., Viraraghavan, T., 2001. Fungal decolorization of dye wastewaters: a review. Bioresource Technology 79, 251–262.

Hai, F.I., Yamamoto, K., Fukushi, K., 2006. Development of a submerged membrane fungi reactor for textile wastewater treatment. Desalination 192, 315–322.

Hai, F.I., Yamamoto, K., Fukushi, K., 2007. Hybrid treatment systems for dye wastewater. Critical Reviews in Environmental Science and Technology 37, 315–377.

Hai, F.I., Yamamoto, K., Fukushi, K., Nakajima, F., 2008a. Fouling resistant compact hollow-fiber module with spacer for submerged membrane bioreactor treating high strength industrial wastewater. Journal of Membrane Science 317, 34–42.

Hai, F.I., Yamamoto, K., Nakajima, F., Fukushi, K., 2008b. Removal of structurally different dyes in submerged membrane fungi reactor–biosorption/PAC-adsorption, membrane retention and biodegradation. Journal of Membrane Science 325, 395–403.

Hai, F.I., Yamamoto, K., Nakajima, F., Fukushi, K., 2009. Factors governing performance of continuous fungal reactor during non-sterile operation - the case of a membrane bioreactor treating textile wastewater. Chemosphere 74, 810–817.

Hao, O.J., Kim, H., Chiang, P.-C., 1999. Decolorization of wastewater. Critical Reviews in Environmental Science and Technology 30, 449–505.

Hunger, K., Gregory, P., Miederer, P., Berneth, H., Heid, C., Mennicke, W., 2004. Important Chemical Chromophores of Dye Classes. Wiley-VCH Verlag GmbH & Co. KGaA.

Isık, M., Sponza, D.T., 2004. Monitoring of toxicity and intermediates of C.I. direct black 38 azo dye through decolorization in an anaerobic/aerobic sequential reactor system. Journal of Hazardous Materials 114, 29–39.

Kapdan, I.K., Tekol, M., Sengul, F., 2003. Decolorization of simulated textile wastewater in an anaerobic–aerobic sequential treatment system. Process Biochemistry 38, 1031–1037.

Knackmuss, H.-J., 1996. Basic knowledge and perspectives of bioelimination of xenobiotic compounds. Journal of Biotechnology 51, 287–295.

Laugero, C., Sigoillot, J.C., Moukha, S., Frasse, P., Bellon-Fontaine, M.N., Bonnarme, P., Mougin, C., Asther, M., 1996. Selective hyperproduction of manganese peroxidases by *Phanerochaete chrysosporium* l-1512 immobilized on nylon net in a bubble-column reactor. Applied Microbiology and Biotechnology 44, 717–723.

Lourenco, N.D., Novais, J.M., Pinheiro, H.M., 2000. Reactive textile dye colour removal in a sequencing batch reactor. Water Science and Technology, 321–328.

Méndez-Paz, D., Omil, F., Lema, J.M., 2005. Anaerobic treatment of azo dye acid orange 7 under fed-batch and continuous conditions. Water Research 39, 771–778.

Manu, B., Chaudhari, S., 2003. Decolorization of indigo and azo dyes in semicontinuous reactors with long hydraulic retention time. Process Biochemistry 38, 1213–1221.

Mezohegyi, G., Kolodkin, A., Castro, U.I., Bengoa, C., Stuber, F., Font, J., Fabregat, A., Fortuny, A., 2007. effective anaerobic decolorization of azo dye acid orange 7 in continuous upflow packed-bed reactor using biological activated carbon system. Industrial & Engineering Chemistry Research 46, 6788–6792.

Mezohegyi, G., Fabregat, A., Font, J., Bengoa, C., Stuber, F., Fortuny, A., 2009. Advanced bioreduction of commercially important azo dyes: modeling and correlation with electrochemical characteristics. Industrial & Engineering Chemistry Research 48, 7054–7059.

O'Neill, C., Lopez, A., Esteves, S., Hawkes, F.R., Hawkes, D.L., Wilcox, S., 2000. Azo dye degradation in an anaerobic-aerobic treatment system operating on simulated textile effluent. Applied Microbiology and Biotechnology 53, 249–254.

Ong, S.-A., Toorisaka, E., Hirata, M., Hano, T., 2008. Granular activated carbon-biofilm configured sequencing batch reactor treatment of C.I. acid orange 7. Dyes and Pigments 76, 142–146.

Rau, J.R., Knackmuss, H.-J., Stolz, A., 2002. Effects of different quinoid redox mediators on the anaerobic reduction of azo dyes by bacteria. Environmental Science & Technology 36, 1497–1504.

Ren, N., Chen, Z., Wang, A., Hu, D., 2005. Removal of organic pollutants and analysis of MLSS-COD removal relationship at different HRTs in a submerged membrane bioreactor. International Biodeterioration & Biodegradation 55, 279–284.

Robinson, T., McMullan, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in textile effluent: a critical review on

current treatment technologies with a proposed alternative. Bioresource Technology 77, 247–255.
Rozzi, A., Malpei, F., Bonomo, L., Bianchi, R., 1999. Textile wastewater reuse in northern Italy (Como). Water Science and Technology 39, 121–128.
van der Zee, F.P., Villaverde, S., 2005. Combined anaerobic–aerobic treatment of azo dyes–a short review of bioreactor studies. Water Research 39, 1425–1440.
van der Zee, F.P., Bisschops, I.A.E., Lettinga, G., Field, J.A., 2002. Activated carbon as an electron acceptor and redox mediator during the anaerobic biotransformation of azo dyes. Environmental Science & Technology 37, 402–408.
You, S.-J., Damodar, R.A., Hou, S.-C., 2010. Degradation of reactive black 5 dye using anaerobic/aerobic membrane bioreactor (MBR) and photochemical membrane reactor. Journal of Hazardous Materials 177, 1112–1118.