Unbiodegradable Soluble COD Removal from Industrial Wastewater by a Hybrid Moving Bed Biofilm Reactor

Carucci A.[1,2], Cappai G.[1,2], Camedda C.[1], Erby G.[1], Puggioni G.[1], Milia S.[2,*], Tocco G.[1]

[1] University of Cagliari – Department of Civil-Environmental Engineering and Architecture (DICAAR), Via Marengo 2 - 09123, Cagliari – Italy

[2] National Research Council of Italy - Institute of Environmental Geology and Geoengineering (CNR-IGAG), Via Marengo 2 - 09123, Cagliari – Italy

*corresponding author: smilia@unica.it

Abstract

In this study, plastics industry wastewater (PIWW) characterized by high total and soluble chemical oxygen demand (tCOD and sCOD, up to ~2200 and ~1500 mg/L, respectively) and remarkable unbiodegradable soluble COD (usCOD, 508±224 mg/L, 31±14% of tCOD) concentrations was treated at laboratory scale using a hybrid moving bed biofilm reactor (MBBR). Interestingly, the MBBR showed average tCOD, sCOD and usCOD removal efficiencies of 26±6, 32±11 and 36±11%, respectively, which were comparable to those achieved by the coagulation/flocculation pre-treatment currently applied at full-scale. Such results encourage the application of MBBR as a cost-effective option for the removal of recalcitrant soluble organics from PIWW and other similar industrial wastewaters.

Keywords: industrial wastewater, MBBR, plastics industry, recalcitrant organics, usCOD

1. Introduction

Moving bed biofilm reactors (MBBRs) can be nowadays considered a well-established process in the field of biological municipal and industrial wastewater treatment. In hybrid MBBRs, biofilm attached to moving plastic carriers coexists with suspended biomass: such systems have been proposed as a valid solution, for example, for upgrading existing activated sludge plants (Mannina et al., 2009). Among industrial effluents, plastics industry wastewater (PIWW) is characterized by high concentrations of total and soluble chemical oxygen demand (tCOD and sCOD, respectively), as well as by remarkable unbiodegradable soluble COD (usCOD) content, the latter often requiring a dedicated removal step. In this study, the feasibility of a hybrid MBBR as an option for effective usCOD removal from PIWW was investigated, and compared with conventional treatments like coagulation/flocculation process (C/F).

2. Materials And Methods

2.1. Plastics industry wastewater

The PIWW (**Table 1**) originated from two different industrial processing methods, namely 'Standard' and 'Green': it is currently pre-treated at the industrial wastewater treatment plant (WWTP) of Porto Torres (Italy) by C/F in order to reduce the usCOD fraction, and mixed with other industrial effluents before undergoing biological treatment by conventional activated sludge. From day 63 of MBBR operation, PIWW was amended with a proper amount of P buffer in order to avoid limiting conditions.

Table 1. Average Standard and Green PIWW composition

Parameter	UM	Standard	Green
tCOD	mg/L	1708±101	1815±387
sCOD	mg/L	1329±141	1219±266
usCOD	mg/L	735±168	646±145
NH_4^+-N	mg/L	12±5	11±5
PO_4^{3-}-P	mg/L	n.d.	n.d.
pH	-	7.4±0.1	9.3±0.7

2.2. Hybrid MBBR design and operation

The hybrid MBBR consisted of a glass vessel with an apparent working volume (*i.e.*, the volume of the liquid phase) of 3 L, filled with 0.2 L AnoxKaldnes K3 carriers (Veolia), and a resulting total working volume of 3.2 L. The MBBR was operated as a sequencing batch reactor (SBR), and mixing was provided through intense aeration. The applied hydraulic retention time (HRT) and organic loading rate (OLR) are reported in **Table 2**.

Table 2. Synthesis of MBBR main operating parameters

Time d	HRT h	N° cycles/day	OLR tCOD g/(L·d)		OLR sCOD g/(L·d)	
			min	max	min	max
0-31	24	2	1.7	1.9	1.2	1.3
32-264	12	4	2.6	4.4	1.7	3.1

The reactor was inoculated twice (day 0 and 32) with activated sludge collected from the industrial WWTP of Porto Torres. From day 118, the suspended biomass sludge age was controlled and kept at 20.

2.3. *Analytical methods*

Determination of COD, total suspended solids (TSS) and volatile suspended solids (VSS) was performed according to Standard Methods (APHA, 2005). Soluble COD was determined according to Mamais et al. (1993).

2.4. *Batch tests*

Batch tests were carried out in duplicate to determine usCOD concentration in MBBR influent and effluent, using unacclimated activated sludge drawn from the municipal WWTP of Cagliari (Italy). The total suspension volume was 0.8-1.0 L, and the applied food to microorganisms ratio was 0.1 g_{tCOD}/g_{SSV}. After 24 hour aeration, the supernatant was collected for sCOD determination. The usCOD concentration ($usCOD_{WW}$) was calculated as follows:

$$usCOD_{WW} = [sCOD_{mix} - sCOD_{blank}]\frac{V_{AS} + V_{WW}}{V_{WW}}$$

Where $sCOD_{mix}$ and $sCOD_{blank}$ refer to analytical determinations of sCOD using MBBR influent/effluent and distilled water (blank), respectively.

Batch tests were also carried out to assess the contribution of volatilization (abiotic), attached and suspended biomass to tCOD, sCOD and usCOD removal.

3. Results And Discussion

Despite the high variability of the different stocks' characteristics, the MBBR showed fairly good performance in terms of removal of the COD fractions considered (**Figure 1A**). In particular, the MBBR was able to remove tCOD, sCOD and usCOD at 26±6%, 32±11% and 36±11%, respectively. As to usCOD, removal efficiencies were comparable with those achieved at full-scale via C/F process. Although process reliability with fluctuating organic loads represents an important advantage of MBBRs (Andreottola et al., 2000), such behavior had been never investigated with industrial wastewater containing high amounts of recalcitrant soluble organics, and specifically focusing on usCOD. Batch tests performed with only suspended or attached biomass revealed that they contributed equally to usCOD removal (37.5 and 35.1%, respectively). Such values were similar to those achieved in the MBBR, which likely represented the highest achievable usCOD removal. Abiotic COD removal through volatilization was found to be negligible (data not shown), therefore biofilm and suspended biomass were considered as the key players in usCOD removal, likely due to a combination of biological and physical (i.e., adsorption) removal patterns. As shown in **Figure 1B**, the amendment of PIWW with phosphate buffer (day 63) enhanced biomass development into the MBBR, thus confirming the need for P supply in the perspective of process scale-up.

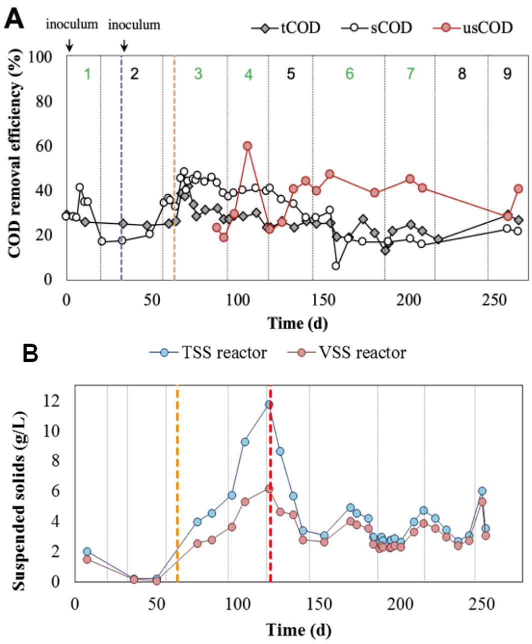

Figure 1. Removal efficiency of the different COD fractions **(A)**, and TSS and VSS trend in the MBBR **(B)**. Green and black numbers refer to 'Green' or "Standard" stocks fed to the MBBR, respectively. Black, purple, orange and red dashed lines indicate separation between different stocks feeding, the decrease of applied HRT, the addition of P buffer to the influent, and the beginning of sludge age control, respectively.

4. Conclusion

The results achieved in this study are comparable with those currently achieved at full-scale through C/F, therefore the use of the MBBR as a cost-effective treatment option (alone, or in combination with C/F in order to achieve higher usCOD removal and lower chemicals consumption at the same time) is strongly encouraged and may be extended to similar industrial wastewaters containing high amounts of recalcitrant soluble organics.

Acknowledgments

The Authors wish to thank the Industrial Provincial Consortium of Sassari for funding this research, and Dr. Graziano Mura and Dr. Matteo Musu for providing precious technical and logistical support.

References

Andreottola, G., Foladori, P. and Ragazzi, M. (2000), Upgrading of a small wastewater treatment plant in a cold climate region using a moving bed biofilm reactor (MBBR) system, *Water Science and Technology*, **41**(1), pp. 177–185.

Mamais, D., Jenkins, D. and Pitt, P. (1993), A rapid physical-chemical method for the determination of readily biodegradable soluble COD in municipal wastewater, *Water research*. Elsevier, **27**(1), pp. 195–197.

Mannina, G. and Viviani, G. (2009), Hybrid moving bed biofilm reactors: An effective solution for upgrading a large wastewater treatment plant, *Water Science and Technology*, **60**(5), pp. 1103–1116, doi: 10.2166/wst.2009.416.