www.water-solutions.info

Issue 3 | 2020

Publishing House:
Vulkan-Verlag GmbH

ISSN: 2509-2731

WATERSOLUTIONS

Water & Waste Water Technologies and Pipeline Construction

Supported by

German Society for
Trenchless Technology e.V.

RESEARCH

Innovative methods and approaches for WFD

RESEARCH

MBR technology, activated carbon and RO coupled to produce water fit for reuse

MBR technology coupled with activated carbon and RO to remove micropollutants and produce water fit for reuse from industrial effluents in North East Brazil

A pilot plant case study

M.C. Martí-Calatayud, C. Bohner, S. Yüce, M. Wessling

Possessing around thirteen percent of the renewable freshwater resources in the world, Brazil is recognized as a water-rich country [1]. Nonetheless, water reserves are unevenly distributed across the Brazilian territory. In particular, the North Eastern states of Brazil enclose one of the largest and most populated semiarid regions in the world: the Semiárido. In contrast with other semiarid regions that are located in the vicinities of desert-like areas, this inland territory is surrounded by humid regions along the Atlantic coast. This peculiarity influences the demography and economy of the Semiárido, which counts with more than 22 million inhabitants. With very low annual precipitations concentrated only within a short span of months, strategies for optimization of water resources in this drought-stricken region are required to consider all types of water use: urban, industrial, and agricultural. BRAMAR, a research project where Brazilian universities and water management entities cooperated with German universities and companies of the water sector, was conceived to introduce technological solutions adapted to the characteristics of NE Brazil, which could contribute to reduce the problems related to water scarcity in the region.

Industrial water reuse: challenges

The implementation of advanced technologies that make feasible the reclamation and reuse of water from so far non-conventional sources, such as industrial effluents, was one of the main aims of the project. In this regard, the most important industrial activities in NE Brazil are related to the textile and agrofood sectors, which are intensive water consumers. The main challenge associated with the reuse of water in the industrial sector derives from the fact that water standards required for such activities are demanding, whereas the generated effluents commonly possess high contaminant loads.

Focusing on agrofood industries, field studies were conducted under the framework of this project in an industrial site located in the city of João Pessoa (State of Paraiba). The industry chosen for the case study was a fruit juice company, which produces fresh and concentrate juice from tropical fruits such as pineapple, cashew, acerola, and mango. The use of water is intensive in the cleaning and peeling of the fresh fruits delivered to the factory. Also, machinery cleaning, refrigeration and evaporative stages make use of water and vapor. The main average properties of the wastewater generated after neutralization and coarse filtration stages are provided in **Table 1**.

Table 1: *Average characteristics of the effluent to be treated in the case study.*

COD (mg/l)	BOD (mg/l)	TOC (mg/l)	N (mg/l)	P (mg/l)	pH	Conductivity (mS/cm)
4004	2426	1475	33.1	17.4	5.27	2.6

Depending on the season and the production capacity, between 10 and 30 m^3/h of wastewater are generated. The most remarkable characteristics of the effluent are the high levels of Chemical Oxygen Demand (COD) above 4000 mg/l and Biological Oxygen Demand (BOD) values around 2500 mg/l. Thus, removal of the high organic load can be highlighted as one of the main objectives of the treatment.
In addition to conventional parameters considered in wastewater treatment, nowadays, there is an increasing concern regarding the presence of micropollutants in the water cycle because of anthropogenic activities. Especially, Brazil is known to be one of the world's leaders in pesticide usage [2]. Because of this massive and often incorrect use of pesticides, surface and groundwater become contaminated due to runoff or leaching from agricultural landscapes [3]. Depending on the origin of the fruits, the presence of pesticides and recalcitrant organics in the fruit skin is also expected in the wastewaters. The presence of micropollutants is a delicate issue, especially when water reuse is intended within the food and beverage sector. Micropollutants are persistent organic molecules difficult to remove and/or degrade, thus implying a risk of accumulation through continuous water reuse cycles.

Field study: removal of organic matter

Biological treatments are cost-effective for effluents highly concentrated in organic matter. However, conventional activated sludge processes (CAS) are not efficient enough to produce water fit for reuse purposes. In this regard, membrane bioreactors (MBRs) arise as an advantageous alternative which combines the physical separation provided by ultrafiltration membranes (UF), with an increased degradation of organic matter by operating at biomass concentrations about threefold of those of CAS plants [4]. An additional advantage of MBR technology is the low footprint associated with small reactor volumes, which is especially interesting in industrial environments.
The company EnviroChemie GmbH in close cooperation with RWTH Aachen University conceptualized a treatment train for the industrial wastewater, where an aerobic MBR was the central stage, preceded by physical pretreatment stages (screen filter, neutralization and electroflotation) and followed by different post-treatments (reverse osmosis, activated carbon filters and ozonation). The pilot plant was commissioned and deployed by EnviroChemie GmbH in the form of a containerized concept. A scheme of the treatment stages is shown in **Figure 1**, while some impressions of the pilot plant can be seen in **Figure 2**. The plant was operated for a year to test the treatment performance in a real industrial environment. The bioreactor was initially seeded with activated sludge from a municipal wastewater treatment plant. After the start-up phase, the concentration of 15 mg/l MLSS was maintained. To conduct the research

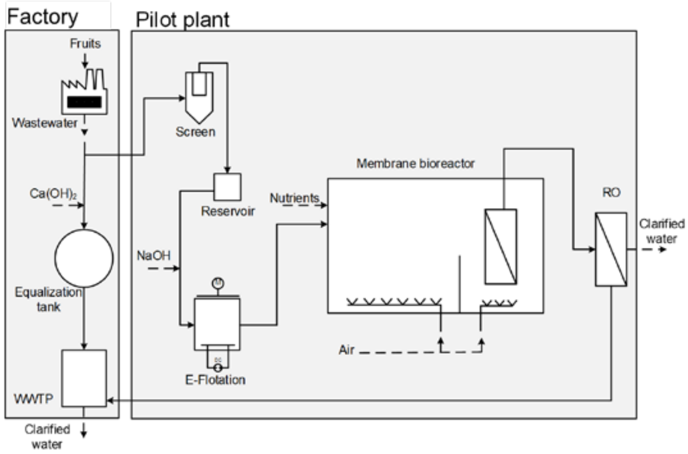

Figure 1: *Flow chart of the pilot plant integrated and connected to the fruit juice producing factory.*

study, approximately 5 m^3/d of the total wastewater generated in the factory was diverted into the pilot plant, while the rest was treated in a CAS plant installed at the industrial site. The MBR was operated with an average permeate flow of 300 l/h in a 10-2 filtration/pause mode; coarse and fine bubble aeration were provided for fouling control and to ensure an oxygen concentration of 2 mg/l in the bioreactor, respectively. The hydraulic retention time was kept at 20 h and the sludge retention time was kept at around 28 days. The transmembrane pressure of the immersed UF module was constantly monitored and registered using a process control system [5].
Results regarding the removal of COD are presented in **Figure 3**, where the evolution of the COD values in the feed of the MBR pilot plant and in the UF-MBR permeate are shown. First, it should be noted that the COD values in the influent wastewater showcase a high variability, which depends mainly on the season of the year and the fruits processed each day. Values as high as 10,000 mg/l COD are commonly measured in the feed. This high variability is very challenging for biological processes. Nonetheless, the results obtained indicate that the COD concentration at the outlet of the UF-MBR lay below 60 mg/l, except for some days mainly at the beginning of the study, which correspond to the initial period of sludge acclimation. Consequently, the daily COD removal efficiency stayed higher than 99%. These results confirm the reliability of MBR technology for treating industrial effluents generated in the food and beverage sector, which usually present high organic loads and wide oscillations in the wastewater quality.
With respect to the removal of nitrogen and phosphorus, in contrast with the common concern of nutrient removal in municipal wastewaters, the industrial wastewater treated in this study presented low concentrations of N and P, as reported in Table 1. Consequently, to ensure a proper COD degradation, urea and phosphorous acid were added as nitrogen and phosphorus source to achieve a COD:N:P

Figure 2: *Impressions about the project BRAMAR and the MBR pilot plant installed by EnviroChemie GmbH in João Pessoa (Paraiba) to treat an industrial effluent coming from a fruit juice producing company.*
a) Trucks transporting drinking water (Carro-pipa) to small towns in the Semiárido,
b) pineapples delivered to the company for the production of juice,
c) view of the containerized MBR pilot plant developed by EnviroChemie GmbH,
d) UF module being introduced in the bioreactor,
e) view from the top of the bioreactor tank, and
f) RO modules.

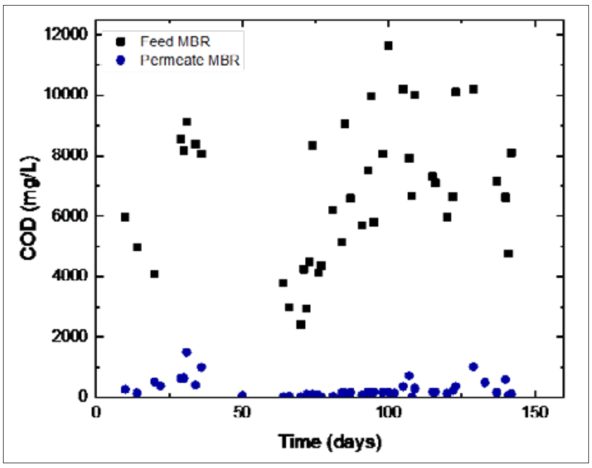

Figure 3: *Evolution of influent and effluent of the MBR over an operating period of 150 days.*

ratio of approximately 200:5:1 in the reactor and provide enough nutrients to the biological tank [6].

Field study: multibarrier solutions to remove micropollutants

The removal of recalcitrant organics was also investigated in the MBR pilot plant. In this case, to conduct a precise study and minimize the effects of incoming effluent variability resulting from the different flows of water, the dependence on the type of fruit being pressed, and the origin of the fruits; four different pesticides were artificially dosed with the influent at constant concentrations of 20 µg/l for 2,4-D, diuron and carbendazim, and 1.5 µg/l for atrazine. The experimental protocol followed in this investigation is presented schematically in **Figure 4**. Basically, three different strategies, each one implemented for periods of two weeks, were compared:

- First, the biological degradation of the four pesticides was evaluated, to check whether the bioreactor conditions are effective in removing the pesticides. The concentration of pesticides in the UF-MBR permeate was monitored on a daily basis by means of LC-MS, so that the temporary evolution of micropollutant removal could be tracked.
- The second experimental series consisted of testing the addition of powdered activated carbon (PAC) in the MBR at a concentration of 0.5 g/l [7]. The PAC was supplied once per week in punctual dosages. The main purpose of this experiment was to confirm if particles of PAC could act as clusters for biofloc formation and increase the retention of pesticides and their biological degradation, so that very small amounts of PAC could induce a significant improvement in micropollutant removal. Only at the end of the first week, when sludge was withdrawn to ensure a biomass concentration of 15 g/l, the portion of removed PAC with the sludge was replenished with fresh PAC.
- Finally, a multibarrier approach consisting of PAC-assisted MBR operation coupled with a reverse osmosis (RO) treatment for the MBR permeate and subsequent recirculation of the RO retentate was investigated. This approach was tested as an alternative way to extend the pesticide retention time in the bioreactor and provide sufficient time to the microorganisms to degrade the micropollutants. Theoretically, this would imply an infinite retention time in the system for pesticide molecules. Preliminary experiments demonstrated rejection rates in the RO unit higher than 90%, but the motivation for returning the retentate was to promote the biological degradation of pesticides, avoiding the need for RO-concentrate management. Since a constant accumulation of pesticides in the bioreactor was expected, the pesticide dosing in the MBR influent was ceased during the second week of this experimental series.

Figure 5 shows an overview of the results obtained regarding micropollutant removal. The ratio between the concentration of pesticides in the MBR permeate and the effluent fed to the MBR (C_{out}/C_{in}) are compared for the four pesticides tested and the three strategies investigated. Since temporary effects such as the acclimation of the biomass to pesticides in the reactor, or saturation of PAC could occur, results for at least two different days within each experimental period are presented. The results regarding the solely biological degradation of pesticides evidence that the hydraulic retention times and the biomass concentration of the pilot plant are not sufficient to reduce the concentration of all pesticides significantly. The results obtained at day 5 and 10 after initiating this experimental series are very similar, hence confirming a stable bioreactor operation. 2,4-D was the most difficult pesticide to degrade, while carbendazim was removed substantially, reaching values of C_{out}/C_{in} of about 0.2. The evolution of pesticide concentration in the MBR permeate indicate that strategies to extend the micropollutant retention time in the bioreactor would be needed to achieve a general degradation of pesticides.

The addition of low amounts of PAC into the bioreactor causes a general improvement in the removal of pesticides. However, if data at different days after the beginning of the experimental series are considered, a temporary effect can be noticed. While at the second day, the C_{out}/C_{in} ratio for atrazine, diuron and carbendazim was lower than 0.2, and more than 50% of 2,4-D was removed; the concentrations of all pesticides in the MBR permeate showed a continued increase at the day 5 and 10 of this experimental series. However, significant differences can be identified between the four pesticides. 2,4-D and atrazine concentrations in the MBR permeate increase faster than the concentrations of diuron and carbendazim. Thus, results confirm that adsorption is the main phenomenon implied in the initial removal observed for 2,4-D and atrazine: the low C_{out}/C_{in} values are temporary and increase with time. On the contrary, a long-term removal of carbendazim and diuron is observed, which could be caused by a synergistic effect between adsorption and biological degradation.

Searching for a general removal for all four pesticides tested, the multibarrier approach consisting of treating the UF-MBR permeate in a RO unit and recirculating the retentate rich in pesticides to the bioreactor was investigated. This was proven to be the most effective approach. Contrary to our initial expectations of a progressive accumulation of pesticides in the bioreactor with their continuous recirculation; using the multibarrier approach, removal rates higher than 90% were obtained for atrazine, diuron and carbendazim. 2,4-D is the most recalcitrant compound among the four tested, although C_{out}/C_{in} ratios lower than 0.3 were also observed for this compound. During the second week of this experimental series, the removal rates continued improving. However, it must be noted that during this week, the pesticide dosing ceased.

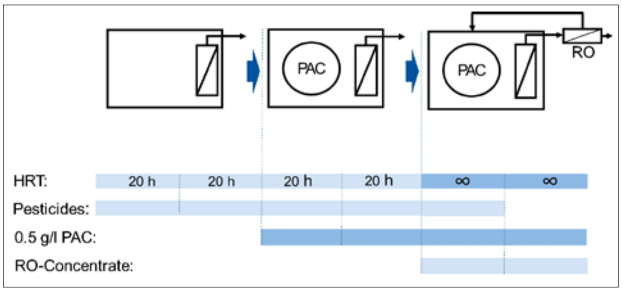

Figure 4: *Scheme of the experimental procedure followed for studying the removal of pesticides in the MBR pilot plant using three different strategies, each one of them tested for 2-week periods: MBR (biological degradation), MBR + PAC (PAC-enhanced biological degradation) and MBR + PAC + RO (PAC-enhanced biological degradation with recirculation of pesticides in RO concentrates).*

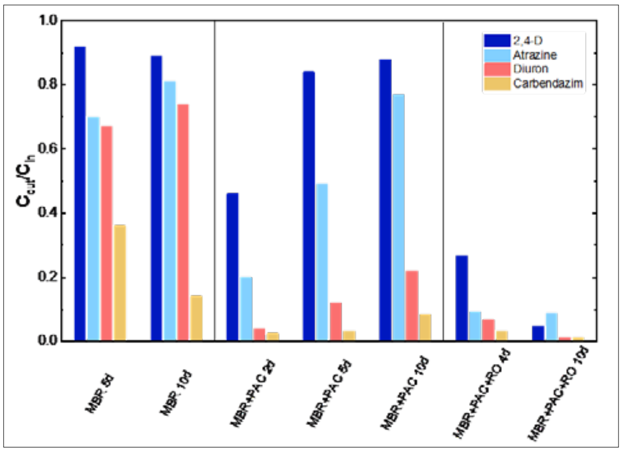

Figure 5: *C_{out}/C_{in} ratios achieved in the pilot plant for the four selected pesticides using different strategies: MBR 5d and 10d refer to the MBR operation at day 5 and 10 after the beginning of the experiment; MBR+PAC 2d, 5d and 10d refer to the MBR operation with PAC dosage at day 2, 5 and 10 after the beginning of the experiment; MBR+PAC+RO refer to the MBR operation with PAC dosage and RO retentate recirculation at day 4 and 10 after the beginning of the experiment.*

Conclusions

The growing population and industrial development of NE Brazil is putting more pressure on water resources. Thus, advanced technological solutions for water treatment and reuse are needed in order to face the increasing challenges of water management in the region. Under the context of the German-Brazilian cooperation project BRAMAR, a pilot plant for treating industrial wastewaters generated in the food and beverage sector was developed and tested onsite in a fruit juice producing factory of João Pessoa (Paraiba). The treatment chain proposed consisted of an aerobic MBR coupled with several post-treatment processes. COD removal rates higher than 99% were obtained in the UF-MBR permeate. Moreover, the achieved results were continued over time, even though the quality of the industrial effluent showed high variability. The removal of organic pesticides artificially dosed to the wastewater was also investigated by using a multibarrier approach, which consisted of the coupling of the MBR technology with PAC dosage and RO filtration. The removal of pesticides depends strongly on their chemical structure. While good biodegradation rates were achieved for diuron and carbendazim, the coupling between several processes is needed to achieve a general removal of micropollutants. The results obtained with the MBR coupled with RO units would allow the reuse of treated water within the industry.

Acknowledgments

This work was supported by the German Federal Ministry of Education and Research (BMBF) through the project BRAMAR (02WCL1334A).

References

[1] Renewable internal freshwater resources, Food Agric. Organ. AQUASTAT Data. (2017). https://data.worldbank.org/indicator/ER.H2O.INTR.K3?end=2014&name_desc=true&start=1962&view=map (accessed October 25, 2020).

[2] S. Rana, A. Beer, R. Birkett, J. Pegg, AGROW World Crop Protection News: Latin America Supplement, Inf. UK. (2015).

[3] S.D. Richardson, T.A. Ternes, Water Analysis: Emerging Contaminants and Current Issues, Anal. Chem. 90 (2018) 398–428.

[4] M.C. Martí-Calatayud, S. Schneider, S. Yüce, M. Wessling, Interplay between physical cleaning, membrane pore size and fluid rheology during the evolution of fouling in membrane bioreactors, Water Res. 147 (2018) 393–402.

[5] M.C. Martí-Calatayud, R. Heßler, S. Schneider, C. Bohner, S. Yüce, M. Wessling, Transients of micropollutant removal from high-strength wastewaters in PAC-assisted MBR and MBR coupled with high-retention membranes, Sep. Purif. Technol. 246 (2020) 116863.

[6] M. Winkler, Optimal nutrient ratios for wastewater treatment Nutrients in activated sludge, Hach Lange. (1997) 1–8. http://www.hach-lange.ma/countrysites/action_q/download;document/DOK_ID/14786173/type/pdf/lkz/MA/spkz/fr/TOKEN/bwHY6wCA68kYX9xFNWsx1uD0UXU/M/8nbj-Q.

[7] M. Remy, P. van der Marel, A. Zwijnenburg, W. Rulkens, H. Temmink, Low dose powdered activated carbon addition at high sludge retention times to reduce fouling in membrane bioreactors, Water Res. 43 (2009) 345–350.

Authors:

Manuel César Marti-Calatayud
Assisant professor
Universitat Politècnica de València,
IEC Group,
Departament d'Enginyeria Química i Nuclear
Camí de Vera s/n
46022 Valencia, Spain
mcmarti@iqn.upv

Dr.-Ing. Christoph Bohner
EnviroChemie GmbH
In den Leppsteinswiesen 9
64380 Rossdorf, Germany

Dr.-Ing. Süleyman Yüce, Prof. Matthias Wessling
RWTH Aachen University
Chemical Process Engineering
Forckenbeckstr. 51
52074 Aachen, Germany