Transients of micropollutant removal from high-strength wastewaters in PAC-assisted MBR and MBR coupled with high-retention membranes

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Abstract

Removal of micropollutants from wastewaters is crucial to ensure safe water reuse and protect natural watercourses. Although membrane bioreactors (MBRs) yield improved degradation of organic compounds, hydraulic retention times are often too short to satisfy acceptable removal rates of recalcitrant organics. Often, results regarding micropollutant removal in treatment plants are susceptible to uncontrolled feed concentrations, which are concomitant to seasonality and consumer habits. In this work, we investigate the concentration transients of four selected pesticides (carbendazim, diuron, 2,4-D and atrazine), which were constantly dosed to a MBR pilot plant treat-

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ing high-strength industrial effluents (COD values $> 4000\ mg/l$). In addition to the regular MBR operation, two feasible means of extending pesticide retention in bioreactors were evaluated: (i) addition of small concentrations of powdered activated carbon (PAC) into the activated sludge and (ii) coupling of the PAC-assisted MBR and a reverse osmosis unit (RO) with recirculation of the retentate. The aim of this work is to provide reliable information on the fate of micropollutants within wastewater treatment plants using different configurations under controlled feed conditions. Results have shown that carbendazim was the only pesticide efficiently ($> 80\%$) removed during regular MBR operation, which has been attributed to the presence of electron donating groups attached to its aromatic ring structure. Improved retention of diuron by addition of PAC enhanced its long-term removal, whereas the effect of PAC addition on the removal of 2,4-D and atrazine was only temporary, thus being mainly attributed to an adsorption effect. Additionally, the function of PAC as platform for biofloc formation limited sludge production and slowed down membrane fouling, further improving the general performance of the MBR. The MBR-RO hybrid process was the most effective one in increasing the residence time of pesticides in the bioreactor, regardless of their functional groups and properties, thus facilitating a generalized removal of micropollutants.

Keywords: membrane bioreactor (MBR), high-strength wastewaters, Powdered activated carbon (PAC), micropollutant removal, Membrane fouling, Reverse osmosis (RO)

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1. Introduction

Water reuse has become an essential practice for ensuring water supply in regions severely stricken by drought events. Also, the preservation of biosphere reserves that are highly vulnerable to climate change rely often on water reuse policies implemented in neighboring urban and industrial areas [1]. Membrane bioreactors (MBRs) are well positioned in this regard, as they are capable of efficiently degrading high organic loads present in wastewaters while involving low space requirements as compared with other technologies [2, 3]. MBRs are especially indicated for production of water fit for reuse purposes. Yet, the introduction of reuse loops is a delicate issue, especially in agrofood industries, where treatment schemes must comply with high quality standards including removal of persistent micropollutants, such as pesticides, hormones and pharmaceuticals. The presence of micropollutants in the water cycle is an emerging threat, as these substances can induce harmful effects on human health [4–6]. Therefore, technological progress and developments are required to tackle the challenge of micropollutant removal in wastewater treatment plants.

Membrane researchers and operators have used different approaches to improve MBR performance, especially in terms of energy consumption, membrane fouling and micropollutant removal [7–9]. Some of these approaches include the modification of membrane surfaces, conditioning of biomass properties or use of hybrid MBR technologies, such as osmotic MBRs and electrochemical MBRs [10–13]. The combination of MBRs and adsorption on

activated carbon has been demonstrated to entail multiple benefits. Remy et al. observed that addition of powdered activated carbon (PAC) improved strength of biological flocs leading to substantial fouling reduction [14]. In addition, improvement in removal of persistent organic compounds by means of adding PAC to activated sludge has been reported [15, 16]. PAC acts as a platform for sludge formation and increases contact between microorganisms and hardly-degradable compounds [17].

The coupling of MBRs and dense membranes in so called high-retention MBRs is another variation which has recently drawn attention of different researchers [18, 19]. Positive effects on organic matter degradation resulting from long retention times of hardly-degradable compounds in bioreactors have been demonstrated [20]. As per micropollutant removal, recirculation of nanofiltration or reverse osmosis (RO) concentrates to MBRs also improved biological degradation [21]. Large sludge retention times (SRT) allowing for better acclimation and biodiversity of microorganisms have been demonstrated to be determinant in the achieved improvements [22–24].

Despite the relevant developments produced in MBR technologies, most research studies on micropollutant degradation are carried out either at lab scale or in treatment plants without controlled conditions with respect to incoming effluent concentrations. Variability in micropollutant concentrations as a consequence of seasonality or anthropogenic habits are known to cause peaks in concentrations of wastewaters [25, 4, 26]. Thus, considering sampling times, transients in different treatment steps and hydraulic retention

times (HRT) are essential in order to get clear information on the real fate of micropollutants within treatment plants. In the following work, the removal of selected pesticides in an aerobic MBR treating an industrial effluent with and without addition of PAC is assessed. Controlled feed conditions by continuous dosage of micropollutants and monitoring transients of effluent concentrations are carried out in order to distinguish different mechanisms of pesticide removal in hybrid MBRs including PAC addition and recirculation of RO concentrates.

2. Experimental

2.1. Industrial wastewater and MBR pilot plant

The present investigation was conducted in a fruit juice producing company situated in the city of João Pessoa (State of Paraíba, Brazil). The factory produces juice concentrates of tropical fruits. The wastewater generated at the company principally originates from fruit rests and machine cleaning operations and does not contain domestic wastewater. To evaluate the potential of MBR technology for treating industrial effluents and its efficiency in micropollutant removal, the company EnviroChemie GmbH (Germany) developed and commissioned a pilot plant consisting of a pre-treatment train, an aerobic MBR and a RO unit as polishing step. All treatments were installed in a shipping container and brought to the industrial site. A simplified flow diagram of the pilot plant is shown in Fig. 1. The pre-treatment includes a bag filter, a mixing pipe where pH neutraliza-

tion and pesticide dosing can take place, and an electroflotation unit. The MBR system consists of a 5 m^3 tank filled with activated sludge, where a flat sheet membrane module with a membrane area of 25 m^2 was immersed (siClaro FM622, Martin Membrane Systems). The membrane is made of polyethersulfone (PES) and has a MWCO of 150 kDa. An eccentric pump (ASV Stübbe, F30 DS) provided the negative pressure for the filtration unit. Aeration was supplied by three compressors with a capacity of 20 m^3/h of air each. The RO filtration system consists of two spiral wound RO-modules (Toray, TML10D) each with 7 m^2 membrane surface area. The membrane is made of crosslinked fully aromatic polyamide. Both modules are linked in cross current circuitry, where a centrifugal pump (Grundfos, CRN 3-17) is used to generate the required pressure.

The wastewater generated at the fruit juice company (approx. 35 m^3/d) is acidic ($\approx$ pH 4). To adjust the pH, the company adds calcium hydroxide before the water enters an equalization tank (850 m^3), where some uncontrolled biological degradation may already occur. From there, wastewater is fed into the MBR pilot plant. During the whole period of this study, the mean chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP) of the wastewater fed to the pilot plant were 4004±698, 33.1±4.55 and 17.4±6.53 mg/l, respectively. These and additional characteristics of the wastewater are presented in Table 1. An analytical screening of pesticides was conducted prior to starting the dosage of pesticides into the MBR pilot plant, from which it was found that the concentration was below

Table 1: Characteristics of the wastewater at the entrance of the MBR.

COD [mg/l]	BOD [mg/l]	TOC [mg/l]	TN [mg/l]	TP [mg/l]	pH	Conductivity [mS/cm]
4004±698	2426±330	1475±25	33.10±4.55	17.40±6.53	5.27±0.23	2.60±0.36

0.12 µg/l for all four pesticides investigated within this study.

Permeate flow (MBI Flowmax 44i) and transmembrane pressure (Endress+Hauser PMD75) were constantly measured. The permeate flow was set to 300 l/h. With filtration cycles consisting of 10 minutes of filtration and 2 minutes of relaxation, the HRT could be set to 20 hours. The aeration supply of the biology was controlled to achieve an O_2 concentration of 2 mg/l, while membrane aeration was maintained at 20 m^3/h. Waste sludge was discarded regularly to reach a mean MLSS value of 15 g/l, leading to a SRT of 28 days. The operating parameters of the RO during the experiment with concentrate recirculation were the following: feed flow of 260 l/h, concentrate flow of 100 l/h and retentate flow of 160 l/h, making up a recovery rate of 61% with transmembrane pressures ranging between 4.3 and 8.9 bar. The MBR permeate flow, the feed, permeate and concentrate flow of the RO unit and the air supply were controlled with a SIMATIC PCS 7 process control system and operated via WinCC. The process data was saved every minute and exported using ACRON reporter.

The UF membranes were cleaned ex-situ in a cleaning chamber outside the MBR. The cleaning basin was filled with the cleaning chemicals, while membrane aeration ensured good mixing and scouring of the membrane sur-

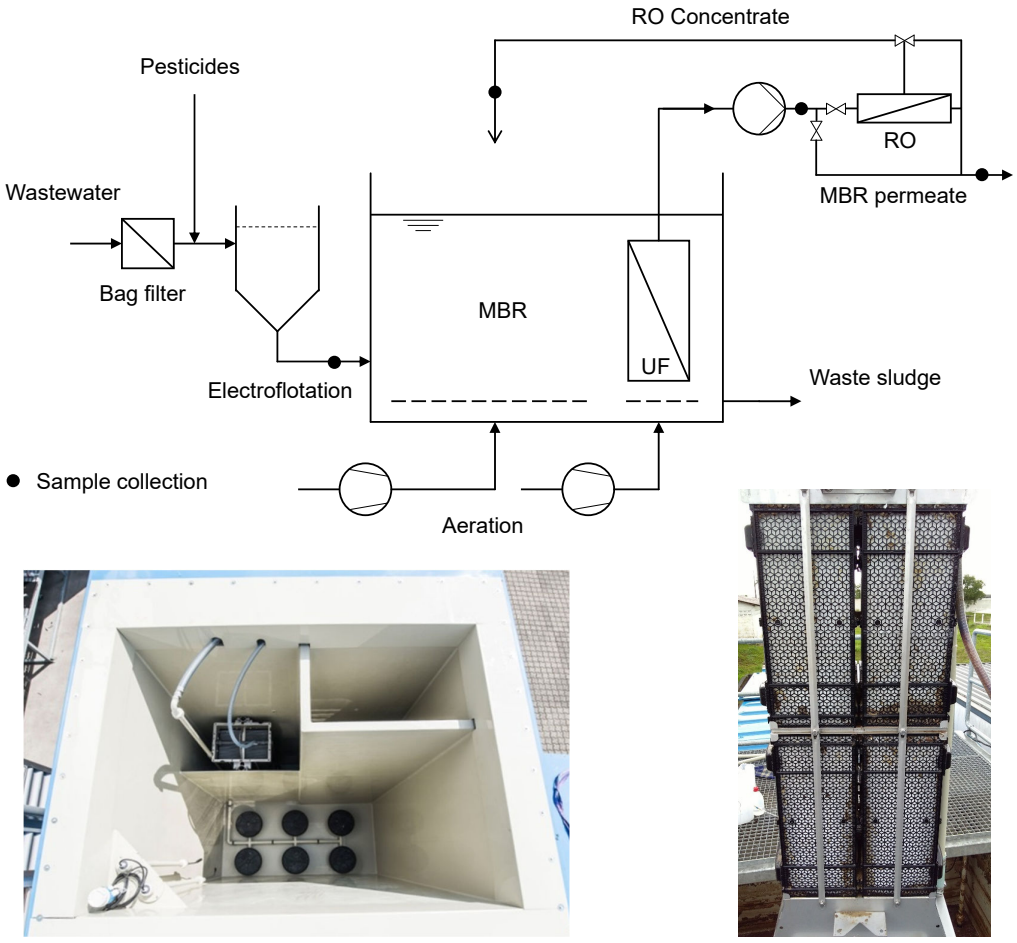


Figure 1: Schematic flow diagram of the MBR pilot plant with inset pictures of the bioreactor embedded in the container and the UF module while being immersed in the MBR after a chemical cleaning.

face. Two different chemical agents were used for the cleaning: first citric acid at pH 3 was used to remove gel layers possibly formed at the membrane surface. Then, NaClO at a concentration of 400 mg/l was used as oxidizing agent. Membrane filtration was performed during the cleaning steps to ensure the access of cleaning agents into the membrane pores. Before, in between and after all cleaning steps, the membranes were rinsed and submerged with abundant water to avoid contamination of the activated sludge.

2.2. Materials

The four pesticides used in this study were 2,4-Dichlorophenoxyacetic acid (usually called 2,4-D; MP Biomedicals, LLC), carbendazim (Sigma Aldrich GmbH), diuron (Sigma Aldrich GmbH) and atrazine (Cayman Chemical Company), which are commonly used in Brazil. A solution of 200 mg/l of 2,4-D, carbendazim and diuron each and 15 mg/l of atrazine was prepared using bioethanol (Etanol comum, ANP No 3/2011). This solution was diluted 1:10 with tap water to achieve concentrations of 20 mg/l and 1.5 mg/l respectively in the pesticide stock solution.

PAC produced from coconut endocarp at the *Laboratório de Carvão Ativado* of the UFPB was used. The PAC has a BET surface area of 823.37 $m^2\,g^{-1}$ and a micropore surface area of 604.67 $m^2\,g^{-1}$. More details on the BET characterization of the PAC can be found in the Appendix A.

2.3. Experimental procedure

The experiments reported in the present work were conducted during a total operation period of 9 months divided in the following phases:

- A 'start up' phase during 165 days without addition of PAC or pesticides, which was used for general observation of MBR operation indicators such as membrane permeability and assessment of COD removal.

- A second phase lasting for 32 days, where the pesticide stock solution was added proportionally to the MBR-feed to achieve a constant feed concentration of 20 µg/l of 2,4-D, carbendazim and diuron each, and 1.5 µg/l of atrazine. During this period, the MBR was operated 24 h per day, with a HRT of 20 h. Sludge was withdrawn only at the beginning of each week. After this second phase, a cleaning of the membrane was conducted.

- A third phase (15 days) involving addition of pesticides into the feed and the addition of PAC directly into the bioreactor to achieve a constant concentration of 0.5 g/l. As in the previous weeks, the MBR was operated with a HRT of 20 h. In the beginning of each week, after withdrawal of waste sludge, the lost PAC was replenished to keep 0.5 g/l PAC in the bioreactor.

- A fourth phase (15 days) of PAC-assisted MBR operation coupled with the RO unit, where the complete MBR-permeate was fed to the RO

and the RO-concentrate was recirculated into the MBR (see Fig. 1). Assuming high pesticide retention during RO filtration, this implies the return of non-removed pesticides to the bioreactor and should result in very long micropollutant residence times in the MBR. Since operation of the RO unit was not possible overnight, the pilot plant was operated only for 8 h a day in continuous mode and 16 h in batch mode (with aeration to maintain biological activity but without feed and permeate flow), making an average HRT of 60 h. To avoid the buildup of large concentrations of pesticides, they were only added to the MBR-feed in the first week of MBR-RO operation. During the second week of RO operation, the concentrate was also recirculated into the MBR and the biological degradation of pesticides was further evaluated.

The target concentrations of pesticides artificially set in the feed wastewater were selected according to typical values found in the literature [4], but also to be below the discharge limits established by the Brazilian legislation. The concentration of 0.5 g/l of PAC added to the activated sludge was chosen based on a previous lab scale research conducted by Remy et al., where this concentration was proven to produce positive effects on membrane fouling and floc conformation without implying increased production of biomass [27].

Adsorption experiments were conducted in the laboratory to assess adsorption capacity of the used PAC for the target pesticides. The adsorption of pesticides was evaluated using two different matrix solutions, distilled water

(pH 6.5) and industrial wastewater collected at the entrance of the bioreactor, after the pretreatment steps (composition shown in Table 1). Solutions of 20, 200 and 2000 20 $\mu g/l$ of 2,4-D, atrazine, carbendazim and diuron and 0.5 g/l activated carbon were mixed in Schott bottles and shaken in an orbital shaker for 24 hours at 25$^{\circ}C$ degrees. Initial concentrations of the pesticide solutions and concentrations of the same solutions after the adsorption experiments were analyzed following the procedure described in Appendix B. The loading of the activated carbon was calculated from the concentration difference between the initial and the final solution. Three repetitions were performed for each experiment.

2.4. Sampling and analysis

Samples for pesticide analysis were taken 5 minutes after the start of a filtration cycle. Double samples were taken and analyzed in some cases in order to corroborate the reproducibility of the analytical measurements. The analysis of pesticides was performed in line with the procedure of Donato et al. [28], who developed a multiresidue method for pesticide analysis, including the ones investigated in this work. More specific information about these procedures is available in the Appendix B.

3. Results and discussion

3.1. Preliminary adsorption experiments

Adsorption experiments were conducted with mixtures of all four pesticides with three different initial concentrations using two matrix solutions:

distilled water and industrial wastewater composed mainly of tropical fruit juice. Fig. 2 shows the adsorption isotherms obtained at $25°C$. Results obtained for the lowest concentration of pesticides ($c_0 = 20\ \mu g/l$), which resembles the composition of the MBR influent, show that all pesticides are adsorbed almost completely on the activated carbon. As the initial solution concentration is 10-fold increased, the solution equilibrium concentration (measured after 24 h) increases somewhat for all pesticides, but more markedly for atrazine and 2,4-D. For an increase in initial concentration corresponding to 100-fold the real concentration of pesticides in the effluent, saturation of activated carbon is already observed. Nonetheless, the solution equilibrium concentration is one order of magnitude higher for 2,4-D and atrazine. These results indicate a much better adsorption of diuron and carbendazim on the activated carbon.

Results obtained with the real wastewater show similar trends, although the equilibrium concentrations in the solution are significantly shifted toward higher values as compared with distilled water. The adsorption of pesticides clearly decreases by an increased affinity with the sugars and other dissolved organic compounds present in the wastewater, or due to screening of active adsorption sites. In this case, 2,4-D shows the lowest adsorption rates on the activated carbon, followed by atrazine.

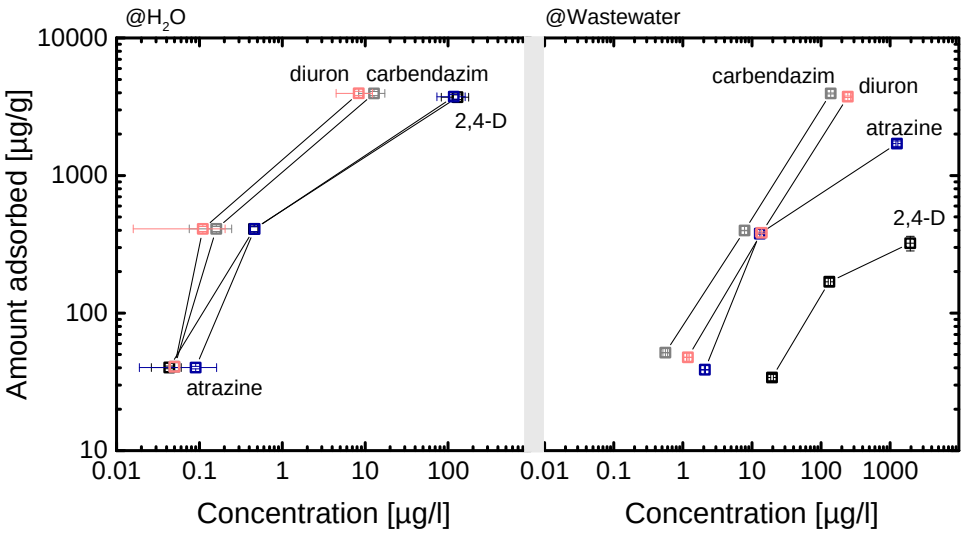


Figure 2: Adsorption isotherms obtained with mixtures of four pesticides in distilled water (left) and MBR feed wastewater (right).

3.2. Removal of pesticides during regular MBR operation

Results of the biological degradation of pesticides collected during two weeks of MBR operation are shown in Fig. 3. After starting the dosing of pesticides, a fast increase in the concentration of the four compounds took place during the first three days. After the third day (day 168 of operation), the concentrations evolved differently depending on the type of pesticide. The lowest removal efficiency was observed for 2,4-D, with a very stable outlet concentration close to that of the feed wastewater. Similar trends were registered for atrazine and diuron, although showing moderate removal rates. For these pesticides, relative concentrations in the effluent (c/c_{Feed}) between 0.65 and 0.81 were reached. The concentration transient of a continuous

stirred tank reactor (CSTR) without reaction term is plotted in the graph for comparison purposes. The evolution of concentration of 2,4-D matches quite well with that predicted for a CSTR, confirming the minimal removal of this pesticide in the MBR. Finally, the results obtained for carbendazim indicate that significant removal (either by biodegradation or by biosorption) took place, since the relative concentration at the outlet lies within 0.14 and 0.36. After the first week, the bioreactor was operated in batch mode with aeration for a period of 16 days, during which the membranes were chemically cleaned ex situ. After this break without permeate extraction nor wastewater inflow, the MBR was operated again for a week (days 187-191) under the same conditions as during the first one. The evolution of concentrations in the effluent is similar to that observed during the first week, hence confirming the trends regarding concentration transients of the four investigated pesticides in the MBR.

Despite the differences in removal rates between compounds observed during the regular operation of the MBR, the low concentrations measured at the beginning of the second week of experiments (day 187) evince that the four investigated pesticides can be biodegraded under specific conditions, namely, if sufficient time is given to the biological community present in the sludge, and if this is exposed to a lack of organic nutrients. Table 2 shows the chemical formula, some properties and Biowin indicators of the four investigated pesticides. Biowin indices are estimates of the aerobic and anaerobic biodegradability of organic chemicals obtained from models developed by the

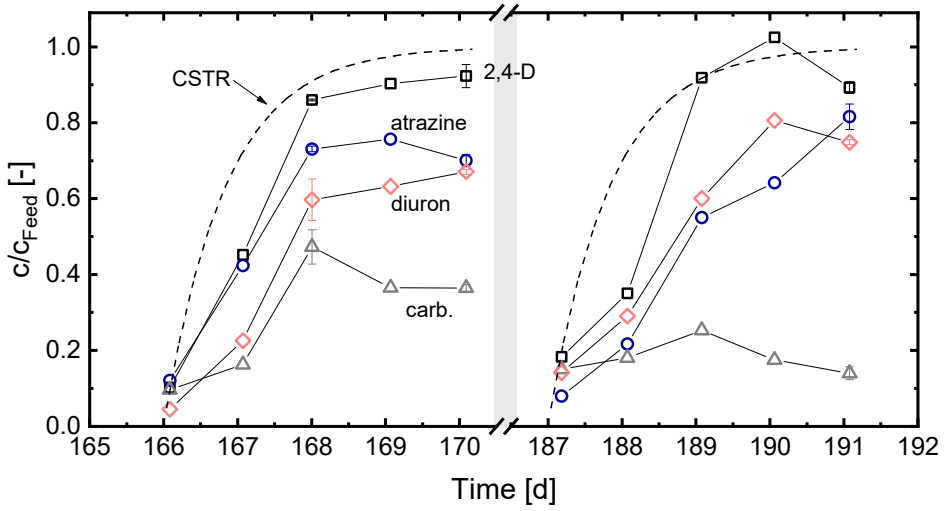


Figure 3: Pesticide removal during the operation of MBR without addition of PAC.

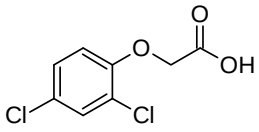
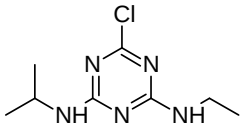
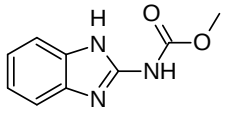
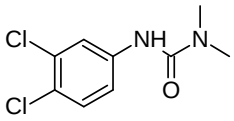
United States Environmental Protection Agency (US EPA). These models are based upon the contribution of functional groups present in each compound [29]. The Biowin 4 indices summarized in Table 2 are estimates of the time needed for primary aerobic biodegradation of organic micropollutants. The four substances treated in this study have indices in the range 3-4. Values of 3 correspond to a primary degradation time of weeks, while values of 4 indicate an expected primary degradation time of days. Accordingly, the removal efficiency observed for the four pesticides investigated in our study agrees well with the Biowin 4 predictions. Unfortunately, treatment times in the range of those had during the interruption period are not practicable for treating large flows of wastewater in a swiftly manner in conventional treatment plants. Here, we also want to remark that in the present study only

the loss of the parent structure of the molecules was considered. According to the estimates of Biowin 3, which predict the expected time for complete mineralization of the pesticides, a period between weeks and months would be needed to achieve ultimate biodegradation of pesticides.

Regarding the removal rates obtained operating at a HRT of 20 h (transients shown in Fig. 3), important differences between the four pesticides were obtained. Several studies have dealt with degradation rates of organic micropollutants in wastewater treatment plants, being hydrophobicity of the organic molecules, toxicity of functional groups and chemical reactivity of organic substituents in aromatic rings considered as relevant factors determining biodegradation rates [30]. The four pesticides analyzed in the present study have similar molecular weight (MW) and hydrophobicity, except carbendazim, which is significantly more hydrophilic. Nonetheless, all four contaminants fall outside the so-called 'removal envelope', that categorizes compounds with log D$>$ 3.2 [31]. The 'removal envelope' is formed by a group of organic molecules which are hydrophobic and show very good biodegradability. Such rapid removal rates are usually associated with biosorption, which ultimately leads to improved biodegradation in MBR sludge as well as to removal by means of periodic purge of excess sludge [32, 23].

Within the group of micropollutants with log D$<$ 3.2 (outside the 'removal envelope'), characterized by showing negligible to low sludge accumulation, researchers have identified evident trends based on the presence of functional groups that can explain to a certain extent different removal rates reported

Table 2: Structure, properties and estimated aerobic biodegradability of the investigated pesticides by the Biowin software. Biowin are estimates of the biodegradability of organic compounds based on the properties of their functional groups. Biowin 1 estimates the biodegradability of compounds under aerobic conditions based on experimental biodegradation data and ranges from 0 to 1 (1: probability of 1 for fast biodegradation, 0: the compound does not biodegrade fast). Biowin 3 and 4 estimate the time required for complete ultimate and primary biodegradation, respectively, and range between 1 and 5 (5: hours, 4: days, 3: weeks, 2: months, 1: longer than months).

Name	Chemical formula	MW [g/mol]	log D	Biowin 1	Biowin 3	Biowin 4
2,4-D		221	2.81	0.4821	2.60	3.66
atrazine		215.7	2.61	0.0045	2.00	3.09
carbendazim		191	1.52	0.7361	2.73	3.76
diuron		233	2.68	0.2717	2.27	3.18

for aromatic micropollutants. Electron withdrawing groups (EWG) attached to aromatic rings make their chemical structure more stable and decrease reactivity, while electron donating groups (EDG) are substituents which increase the likelihood of aromatic rings of undergoing chemical transformations. Accordingly, organic compounds only having EDG usually show fast biodegradability, compounds only having EWG show very low biodegradability, whereas compounds having both types of groups exhibit variable removal rates [30]. In the present case, carbendazim has a carbamate group bound to an aromatic ring in its structure, thus belonging to the first group of substances (less chemically stable compounds). The good removal rates observed for this pesticide are therefore in good agreement with the biodegradability series classification based on the presence of EDGs and EWGs. Moreover, it also correlates with the high Biowin 1 score for this compound, which indicates a high probability of fast biodegradation (> 0.5). 2,4-D, atrazine and diuron possess both types of substituents, EDG and EWG, in their structure. On the one hand, these three compounds have chlorine attached to their aromatic rings, which is a weak EWG. On the other hand, 2,4-D has an ether, atrazine has two amine groups and diuron has an amide group in their respective structures, all of them possessing electron donating properties. The presence of chlorine as EWG along with its toxicity seem to play a role in the recalcitrant properties of these compounds [33].

3.3. Removal of pesticides during PAC-assisted MBR operation

As seen in the previous subsection, high concentrations of biomass in MBRs are not sufficient to achieve fast degradation of micropollutants. However, increased micropollutant residence times showed a notable improvement in their removal rates. Consequently, addition of PAC to increase the retention of pesticides in the bioreactor seems a proper strategy to improve biodegradation in MBRs. The results obtained when PAC was added to the MBR sludge are shown in Fig. 4. The addition of PAC led to a direct decrease of all pesticide concentrations in the permeate effluent (day 195). This sharp decrease can be principally attributed to an initial adsorption effect on fresh PAC. As the operation time after PAC dosage increases, more pesticides are introduced with the feed, while the concentration of PAC remains constant at 0.5 g/l. Consequently, the adsorption capacity of the activated carbon is reached, and the concentrations of 2,4-D and atrazine increase with time after the second day of operation. Contrariwise, the permeate concentrations of carbendazim and diuron increase very slowly, and are significantly low as compared to those measured during the operation of the MBR without PAC dosing. The same experimental run was repeated after operating in batch mode over the weekend break, during which the fruit juice company does not generate wastewater. For the second week, only the PAC removed during sludge purge was replaced with fresh PAC to keep the total concentration at 0.5 g/l. While the first week 2.4 kg of PAC were dosed, a smaller quantity of fresh PAC (0.625 kg) was added to the bioreactor at the beginning of the

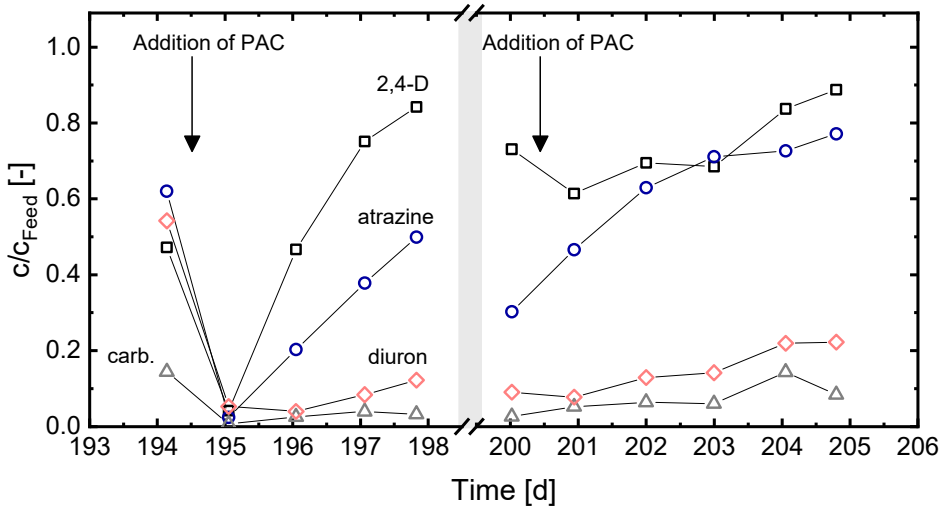


Figure 4: Pesticide removal during the PAC-assisted operation of the MBR.

second week. Hence, the decrease in micropollutant concentration observed at the second day is less noticeable in this case, and only a small decrease can be detected for 2,4-D and diuron.

The PAC-assisted MBR operation thus shows two differentiated trends. The concentration of 2,4-D and atrazine follows a continuous increase during the second week, reaching levels of 77 and 88% of the feed concentration at the last day, respectively. These results illustrate that the effect of PAC for these compounds is temporary and mainly caused by adsorption on the activated carbon. On the contrary, an improved removal of diuron was achieved during the second week, with a prolonged positive effect of the addition of PAC. The same trend was observed for carbendazim, for which removal rates higher than 90% were reached. Clearly, these results show a good agreement

with the preliminary adsorption experiments (cf. Fig 2): the higher adsorption capacity for diuron and carbendazim leads to long-term improvement of their biodegradability. 2,4-D and atrazine which exhibited lower adsorption on PAC, only show a temporary improvement, which fades out for longer operation times. During this experimental period, also a significant degradation of pesticides took place during the weekend break, where the MBR was operated in batch mode neither receiving feed wastewater nor pesticides. Again, the relevance of retention time as well as of competence between pesticides and other organic compounds on the rate of biodegradation of micropollutants are confirmed.

3.4. Removal of pesticides in high-retention PAC-assisted MBR coupled with RO

The preceding experiments showed that when the system was operated with relatively long retention times, e.g. during the weekends, higher degradation rates were observed. Coupling of MBRs with RO units is expected to imply a virtual unlimited retention time for the pesticides. The complete permeate of the MBR was treated with the RO unit with a recovery rate of 60%, where the retentate was returned to the MBR. Results on pesticide rejection by the RO membranes are mostly above 90%, as shown in the Appendix C and in agreement with previous studies [34]. Since the plant was not designed for the RO to be operated overnight, the system was operated in semi-batch mode for two weeks, with a period of 8 h of normal operation dur-

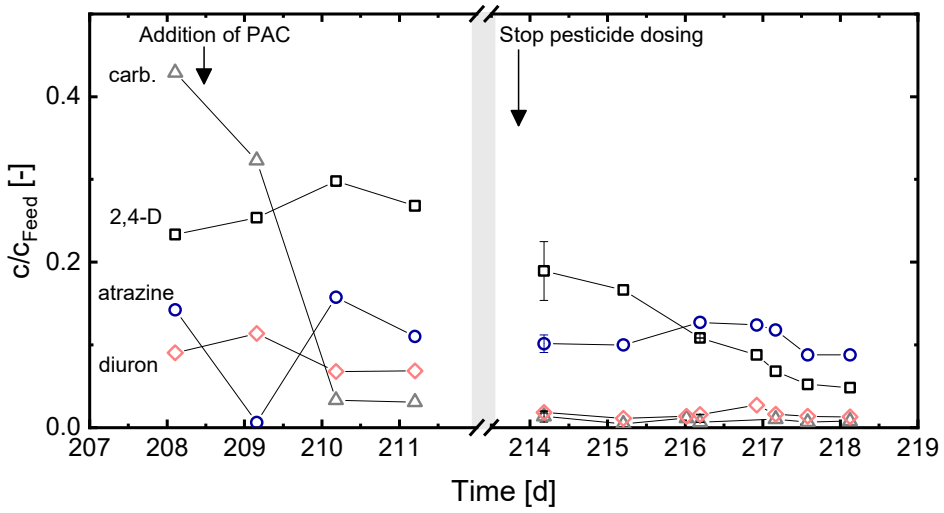


Figure 5: Pesticide removal during the PAC-assisted operation of the MBR coupled with RO in full pesticide retention mode.

ing the day (with continuous feed of wastewater, permeate extraction and recirculation of RO concentrate), and a period of 16 h overnight in batch mode. The resulting average HRT increased to 60 h accordingly.

The results obtained with the RO recirculation are shown in Fig. 5. The PAC lost with sludge withdrawal was replenished with 730 g of fresh PAC at the beginning of the experiments (day 208). However, no clear immediate effect was observed in pesticides' concentrations. Initially, the recirculation of RO-concentrate was expected to lead to an accumulation of pesticides and values of relative concentrations in the MBR permeate higher than 1. Accordingly, the dosing of pesticides was stopped for the second week. Nonetheless, contrary to the initial expectations, the results during the first week showed a significant decrease in pesticide concentration in the effluent (see MBR

permeate to MBR feed relative concentrations shown in Fig. 5). The concentration of carbendazim decreased after PAC addition and remained low. A similar trend was observed for diuron, whereas the values of atrazine and 2,4-D oscillated between 0.1 and 0.3 c/c_{Feed}.

The batch operation during the weekend implied a further decrease of the concentration of all pesticides. During the second week of MBR-RO operation, when the dosage of pesticides was stopped, the concentrations of carbendazim and diuron were mostly below 0.3 $\mu g/l$, which implies a degradation higher than 90%. The degradation of atrazine and 2,4-D took place more slowly and gradually. These two pesticides required longer times until a removal efficiency above 90% was achieved at the end of the week. Again, the longer HRT, which in this experiment is controlled both by the intermittent operation of the MBR and by the recirculation of RO concentrate to the MBR feed, causes a general improvement of the degradation of all pesticides. In addition, the longer residence time of pesticides in the bioreactor may also have contributed to improve biodegradation of all pesticides.

In general, carbendazim was degraded fast in all cases, also with the regular operation of the MBR. The absence of EWG or halogens in its structure along with the development of slow growing nitrifying bacteria may facilitate its degradation. On the contrary, the other pesticides required longer times and benefited from the variations introduced in the MBR configuration. Especially significant is the case of diuron, for which a notable increase in its removal could be induced by adding activated carbon. Nonetheless, the

solely addition of activated carbon was insufficient to improve the removal of atrazine and 2,4-D substantially. The former contains a heterocycle which is completely unsaturated while the latter contains a chlorine substituent in the ortho position respective to the EDG. In conclusion, the present work showed that extending the retention of micropollutants either by improving their adsorption to a substrate or by recirculating the retentate of a dense membrane process such as RO are effective ways for improving their removal in MBRs. In this process, the effluent matrix as well as the operation of bioreactors under conditions of lack of nutrients can significantly affect the efficiency of the treatment process. Research focusing on production of adsorbents with tailored properties, which could show increased adsorption capacities for compounds like 2,4-D and atrazine, is particularly encouraging. Also the possibility of an uncontrolled buildup of micropollutants in MBRs coupled with high-retention membranes and its effects should be treated in detail in future investigations.

3.5. General MBR performance indicators

PAC addition to MBR sludge has been investigated as a fouling mitigation measure in previous works [35]. Remy et al. conducted an extensive investigation to elucidate the most influencing mechanisms that improve membrane permeability and delay critical fouling when low concentrations of PAC are added to activated sludge [27, 14]. Different hypotheses were suggested to explain the observed reduction of membrane fouling: (i) scouring of

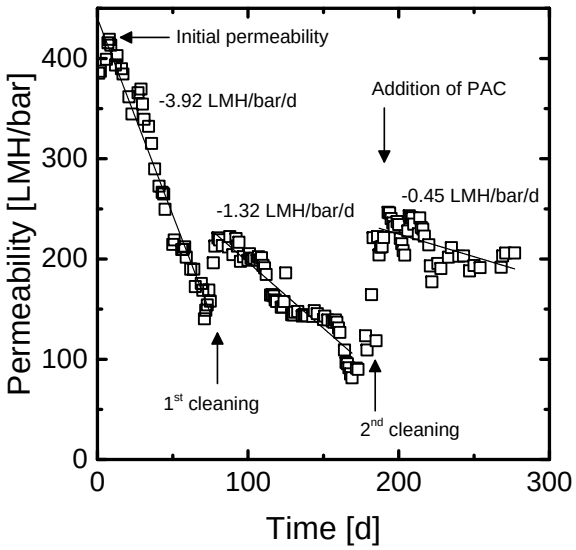


Figure 6: Permeability of the membrane during the experimental period.

the membrane surface by powdered carbon in suspension, (ii) adsorption of critical foulants on activated carbon rendering lower exposure to foulants of the membranes, and (iii) improvement of floc strength on the membrane surface by which less foulants are released. The main conclusion of the above mentioned works pointed to the latter mechanism as the most influential, since contribution of scouring would not be significant at low PAC concentrations and the decrease of COD in the supernatant when PAC was added was not substantial [14].

We monitored the effect of PAC addition on the membrane permeability with the aim of confirming that positive effects on membrane fouling also occur in larger scale MBR systems. Fig. 6 shows the evolution of membrane permeability during 9 months of MBR operation. As mentioned in

the experimental section, the MBR was operated without addition of PAC for 165 days. The membranes had an initial permeability of 400 LMH/bar ($l \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$), which corresponds with an average TMP of 30 mbar. During the first phase of operation, a steep permeability decrease at a rate of 3.92 LMH/bar/day took place. After 80 days of operation the first chemical cleaning of the membranes was performed, where only part of the initial permeability was recovered. The development of irreversible fouling is probably the reason for the moderate permeability recovery observed after the chemical cleaning, as well as for the steep permeability decrease produced during the initial experimental phase [36, 37]. The decay of membrane permeability after the first chemical cleaning was consequently much slower, with a rate of 1.32 LMH/bar/day. When the membrane permeability dropped to 80 LMH/bar (where the TMP took values close to 190 mbar), a second cleaning took place, right before starting dosage of PAC to the bioreactor. The last phase shown in Fig. 6 thus corresponds to the PAC-assisted MBR operation. A notably lower rate of permeability decay of 0.45 LMH/bar/d was registered. Accordingly, the results obtained show that addition of PAC reduced fouling rates. Similar results were reported in previous works, which are in accordance with the low fouling rates achieved by adding PAC to the sludge [38]. In the present study, the improvement in floc strength might be the main reason for the fouling rate reduction. A significant adsorption of extracellular polymeric substances is less likely to happen in microporous PAC, like the one used in the present work (cf. Appendix A), due to size exclusion

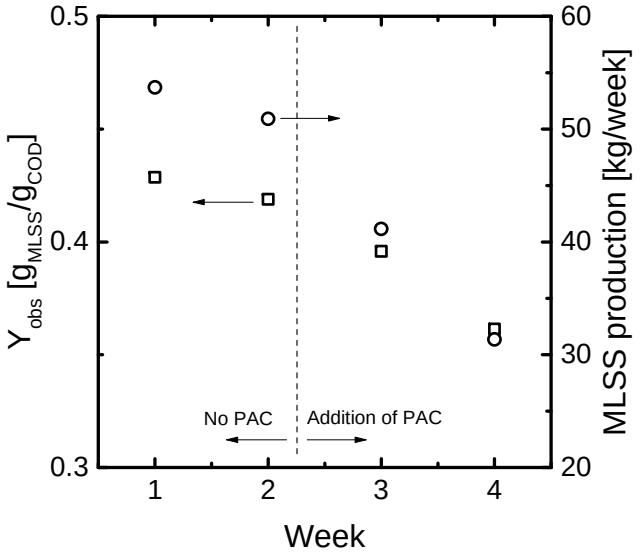


Figure 7: MLSS growth during the two first experimental phases at an HRT of 20 h with and without addition of 0.5 g/l PAC.

effects. Moreover, the industrial wastewater treated in our study had high loadings of organic matter compared to municipal wastewaters, which makes the adsorption of extracellular polymeric substances at low concentrations of PAC even less significant.

A decrease in the growth of biomass because of PAC addition has been also reported in some studies [39, 40]. This is a relevant parameter in MBRs, since sludge management costs can represent a considerable percentage of operational costs. Nonetheless, it has also been reported that excessive addition of PAC can lead to an increase in sludge production as well as an excessive increase in costs related to PAC purchase [41]. The biomass production was also monitored on a weekly basis. Fig. 7 shows the observed

biomass yield, Y_{obs}, which represents the specific biomass formed per mass of substrate consumed in the bioreactor in g_{MLSS}/g_{COD}, corresponding to the four weeks when the HRT was 20 h. During the two weeks without addition of PAC more than 50 kg of sludge were produced, whereas addition of PAC led to a considerable reduction in the net biomass production. If the specific biomass yield is considered, the benefits of adding low concentrations of sludge are confirmed. The obtained results are in line with the works of Lesage et al. and Nguyen et al., who attributed the reduced sludge production to the formation of bioflocs on activated carbon [39, 40]. The formation of bioflocs around particles of activated carbon may cause an insufficient substrate transfer to the internal region of the bioflocs, hence controlling their growth. Consequently, small concentrations of PAC not only reduce fouling in MBRs, but can also induce a reduction in excess sludge production. Importantly, the present work confirmed that the trends already found in experimental works conducted at laboratory scale are extrapolated in a larger scale pilot plant treating industrial effluents with high concentrations of organic compounds.

Regarding side-effects of RO-concentrate recirculation, this change in configuration does not only imply an extended retention of micropollutants in the bioreactor, but it can also induce an increase in the concentration of ions in the biological sludge. The conductivity of the industrial effluent is highly variable, however, the effect of RO-concentrate recirculation on the salt content in the bioreactor could be identified by representing the rate between the

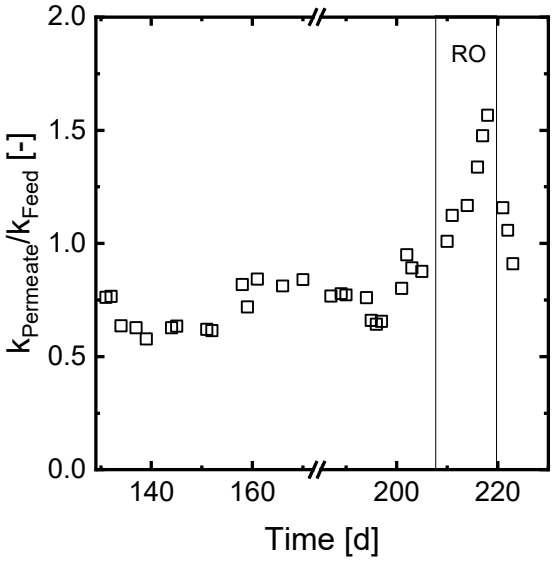


Figure 8: Evolution of the rate between the conductivity in the MBR permeate and in the MBR feed. The period within the two vertical lines corresponds to the MBR-RO coupled operation with recirculation of the RO-concentrate to the bioreactor.

conductivity in the MBR permeate ($k_{Permeate}$) and in the MBR feed (k_{Feed}). Fig. 8 shows the evolution of the conductivity ratio over a long period of operation, including the period when the MBR was coupled with the RO unit. Although this period lasted only for two weeks, a gradual but significant increase in the conductivity ratio took place. When the RO-concentrate is not returned into the MBR, values of $k_{Permeate}/k_{Feed}$ are lower than 1. However, after the two weeks of RO-concentrate recirculation, this ratio reached a maximum value of 1.56. Previous studies have analyzed the effect of increased salinity in MBRs, reporting alterations in the microbial community and membrane performance [42, 43]. However, such remarkable effects were not detected in the present study. This may be caused by the short period of coupled MBR-RO operation. After ceasing the RO-concentrate recirculation, the conductivity ratio decreased to values lower than 1. The effect of salinity buildup in MBRs may suppose an additional challenge for the strategy of coupling MBRs and high-retention membranes. Thus, long-term investigations would be needed to quantify and understand such effects. In this sense, some studies already propose alternatives to overcome the possible negative effects of concentrates recirculation on bioreactor performance, such as the use of halophilic microorganisms or the synthesis of membranes with low salt rejection and high micropollutant rejection [42, 44].

4. Conclusions

In this work, the performance of a MBR pilot plant has been evaluated in terms of micropollutant removal efficiency. Four selected pesticides with different properties and structural features were artificially dosed into high-strength industrial effluents. In addition to the regular MBR operation, two different strategies were tested to increase the retention of pesticides in the bioreactor: (i) PAC-assisted MBR and (ii) coupling of MBR with RO and recirculation of concentrate stream. The main conclusions of our research are summarized as follows:

- The biological removal rates of carbendazim ($> 80\%$) were significantly higher than those achieved for the other pesticides ($< 30\%$). The recalcitrant properties of diuron, 2,4-D and atrazine can be related to the presence of chlorine in their chemical structure.

- The addition of low concentrations of PAC caused an immediate decrease of pesticide concentration in the effluent. However, long-term effects were only observed for carbendazim and diuron, which are preferentially adsorbed on the used PAC.

- Coupling of MBR with RO and recirculation of concentrate was only feasible in semi-batch mode. Yet, this was the most promising MBR configuration allowing for a generalized improvement in pesticide removal rates independently of the type of micropollutant.

- The addition of low concentrations of PAC into the MBR caused additional positive impacts on the performance of the MBR. Membrane fouling rates and sludge production diminished significantly after addition of PAC. These results, obtained treating real effluents in pilot plant scale, are in line with previous studies conducted in the field at lab scale. The main hypothesis behind this positive effect is based on the formation of biofloc clusters around particles of activated carbon, which improve floc strength and diminish the release of foulants.

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Appendix A. BET characterization of the PAC used in the present study

The PAC was analyzed by BET measurements. Table A.3 presents the data of the BET surface area analysis.

Table A.3: Parameters of the powdered activated carbon produced from coconut shell.

	B.E.T.	823.37
Surface area [$m^2\,g^{-1}$]	Micropore	604.67
	External area	218.70
Pore size [Å]	Mean mesopore size	21
Pore volume [$cm^3\,g^{-1}$]	Mean mesopore volume	0.28

Appendix B. SPE and LC/MS procedure for pesticide concentration and analysis

Feed samples were pre-filtered with 0.45 µm PTFE filters to remove solids in the analytes. The pesticides were pre-concentrated by a factor of 100 by means of solid phase extraction and then analyzed by means of liquid chromatography with tandem mass spectrometry. First, SPE cartridges (Waters, Oasis® HLB, 60mg, 3cc) were conditioned with 3 ml methanol (MERCK, HPLC grade) followed by 3 ml distilled water and by 3 ml distilled water previously adjusted to pH 2.5 with phosphoric acid. The pH of the 100 ml samples was also adjusted to pH 2.5 with phosphoric acid ($> 85wt\%$, Dinâmica Ltda.). Subsequently, samples were percolated through the SPE cartridge by a vacuum pump (filtration speed of around 3 drops per second). Afterwards the cartridges were dried under a gentle stream of nitrogen for 20 minutes.

Table B.4: Information on LC-MS/MS for the analysis of pesticides

Compound	ESI	Precursor ion [m/z]	Product ion [m/z]	Recovery [%]
2,4-D	−	218.9	160.9	95.0±0.4
atrazine	+	216.2	174	108.0±8.5
carbendazim	+	192.2	160	88.1±1.0
diuron	+	233.2	71.9	94.8±1.9

The dried cartridges were then eluted with 1 ml of dichloromethane and 1 ml of methanol. The eluate was then evaporated under a gentle nitrogen stream so that only the analyte remained as a solid residue. Finally, the analyte was re-dissolved in 1 ml of mobile phase of the liquid chromatography.

The pre-concentrated pesticide samples were then analyzed by liquid chromatography with tandem mass spectrometry (LC-MS/MS). A Hypersil GOLD column (150 x 2.1 mm, particle size: 5 µm, Thermo Scientific) and a Finnigan LXQ ion trap mass spectrometer were used for the LC-MS/MS. The mobile phase consisted of 5 mmol/l ammonium formate aqueous solution (LiChrosolv, LCMS grade) as solvent A and methanol (Promochem, Optigrade LCMS) as solvent B. The column oven was set to 30 °C and the capillary temperature was 250 °C. The injection volume was 20 µl and the mode of detection was electrospray ionization (ESI). Table B.4 presents further parameters like the ESI mode, precursor ion and product ion for each compound of the analysis by LC-MS/MS as well as their recovery rate.

To calculate the recovery rate of the analytical procedure, a solution of 20 µg/l of 2,4-D, carbendazim and diuron and 1.5 µg/l of atrazine was prepared and analyzed by SPE and LC-MS/MS. This procedure was repeated

three times and its results were compared to the initial concentrations of the solution. Carbendazim showed the lowest recovery rate with 88.1% and atrazine the highest recovery rate with 108%. All analysis results of pesticides in this work were corrected by these recovery rates.

Appendix C. Rejection of pesticides by RO membranes

To verify the assumption of high retention rates of the pesticides in the reverse osmosis and assess its general applicability to remove pesticides, samples of the inlet (MBR permeate), permeate and retentate of the reverse osmosis were taken on day 169 and day 208 and analyzed. Table C.5 presents the corresponding results. The retention R was calculated using the feed and permeate concentrations of each compound i:

$$R_i = 1 - \frac{c_{i,permeate}}{c_{i,feed}} \quad [\%] \tag{C.1}$$

Apart from one sample of carbendazim, retention rates of the reverse osmosis were found to be larger than 90% for all compounds.

Table C.5: Results of reverse osmosis as post treatment on day 169 and 208.

c_{feed} [µg/l]				Retention rate [%]			
2,4-D	Atr.	Carb.	Diuron	2,4-D	Atr.	Carb.	Diuron
17.8	2.5	1.7	7.9	98.5	94.8	84.1	95.7
4.6	0.5	8.9	1.4	97.2	91.5	99.0	91.4

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