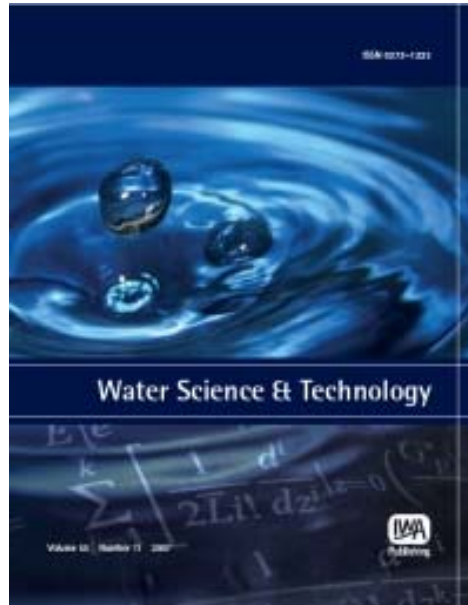


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Reverse osmosis concentrate treatment by chemical oxidation and moving bed biofilm processes

S. M. R. Vendramel, A. Justo, O. González, C. Sans and S. Esplugas

ABSTRACT

In the present work, four oxidation techniques were investigated (O_3 , O_3/UV , H_2O_2/O_3 , $O_3/H_2O_2/UV$) to pre-treat reverse osmosis (RO) concentrate before treatment in a moving-bed biofilm reactor (MBBR) system. Without previous oxidation, the MBBR was able to remove a small fraction of the chemical oxygen demand (COD) (5–20%) and dissolved organic carbon (DOC) (2–15%). When the concentrate was previously submitted to oxidation, DOC removal efficiencies in the MBBR increased to 40–55%. All the tested oxidation techniques improved concentrate biodegradability. The concentrate treated by the combined process (oxidation and MBBR) presented residual DOC and COD in the ranges of 6–12 and 25–41 mg L⁻¹, respectively. Nitrification of the RO concentrate, pre-treated by oxidation, was observed in the MBBR. Ammonium removal was comprised between 54 and 79%. The results indicate that the MBBR was effective for the treatment of the RO concentrate, previously submitted to oxidation, generating water with an improved quality.

Key words | chemical oxidation, MBBR, reverse osmosis concentrate

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INTRODUCTION

Although reverse osmosis (RO) is an established and diffused technology, it generates a concentrated stream that causes environmental impacts if discharged without any treatment (Westerhoff *et al.* 2009). Treatment of RO concentrate, also named retentate and brine, has been the object of some studies. Dialynas *et al.* (2008) investigated several techniques to treat RO concentrate: coagulation, activated carbon adsorption, electrochemical treatment, photocatalysis and sonolysis. Ng *et al.* (2008) utilized biological activated carbon (BAC) and capacitive deionization (CDI) to remove the organic matter and inorganic ions from RO brine. Lee *et al.* (2009) combined ozonation, BAC and CDI to treat RO concentrate. Advanced oxidation processes were combined with biodegradation to remove the organic matter content of a RO concentrate (Westerhoff *et al.* 2009). Electro-oxidation was employed to treat a concentrate containing emerging pollutants (Pérez *et al.* 2010). Advanced oxidation processes were also applied to remove pharmaceutical and personal care products from the retentate of an industrial RO unit (Abdelmelek *et al.* 2011). Although oxidation processes have been used to remove organic matter from RO

concentrate, they can be combined with biological processes to enhance treatment performance. Additional and more sophisticated techniques are necessary when inorganic ions should be removed to acceptable levels.

RO brine may contain recalcitrant organic matter and usually presents low biodegradability, expressed by the low ratio BOD₅/COD (biochemical oxygen demand/chemical oxygen demand). Ozone and hydrogen peroxide can oxidize some recalcitrant compounds originally found in RO brine, improving its biodegradability and rendering the wastewater suitable for biological treatment. Among the biological treatment techniques, the moving-bed biofilm reactor (MBBR) presents some important advantages such as high surface area for biofilm adhesion, high sludge age and robustness.

In the present work, several oxidation techniques (O_3 , O_3/UV , H_2O_2/O_3 , $O_3/H_2O_2/UV$) were investigated to treat RO concentrate. Additionally, the performance of a MBBR fed with RO concentrate, previously submitted to chemical oxidation, was investigated in order to obtain water for reuse, especially in a locale where water stress is intense.

METHODS

The concentrate or retentate used in the present work came from a sewage treatment plant located in Barcelona, Spain. The wastewater from the secondary clarifier of the treatment plant was filtered (sand filtration and membrane microfiltration) before feeding the RO unit. In the sewage treatment plant, the RO permeate is used as reuse water and the concentrate is discharged into the sea. Several samples of RO retentate were collected and transferred to the laboratory during the experimental work. Samples were stored under refrigeration ($<5^{\circ}\text{C}$) until use.

A 2-L oxidation reactor was used in assays operated in a batch mode with the following oxidants: O_3 , O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$. A low pressure mercury lamp (Philips TUV 8W, G8T5, 254 nm), presenting photon flow of $1.5 \cdot 10^{-5}$ Einstein $\cdot\text{s}^{-1}$, was employed in the radiated assays. Ozone dose was $10 \text{ gO}_3 \text{ Nm}^{-3}$, leading to transfer ratios of 9 to $11.5 \text{ mgO}_3 \text{ mg}^{-1}$ DOC (dissolved organic carbon). H_2O_2 concentration was 10 mg L^{-1} in the peroxidation assays. The contact time of the oxidation assays always lasted 20 min. The pH of the retentate was not adjusted and was close to 7. Assays were conducted at room temperature ($19\text{--}23^{\circ}\text{C}$). Figure 1(a) shows the oxidation unit used in the experiments. After oxidation the

RO concentrate was stored under refrigeration and then used to feed the moving-bed reactor.

Two 0.5-L capacity MBBRs were employed, one of them (control) fed with the RO concentrate and the other one fed with the concentrate previously treated by chemical oxidation. Figure 1(b) illustrates the MBBR set-up. The glass reactors contained 40% of their useful volume occupied by the supports (biomedia). Plastic biomedia from Dynamic Aqua Science Inc, type AMD Bio Media™, model MR-01, presenting a specific superficial area of $650 \text{ m}^2 \text{ m}^{-3}$, were employed in the experiments. Air was supplied at the reactor bottom through a porous diffuser to promote oxygen transfer and biomedia circulation inside the reactor. Reactors were operated at room temperature ($19\text{--}23^{\circ}\text{C}$) in parallel for 6 months with a hydraulic retention time of 24 h.

COD and volatile suspended solids (VSS) determinations were made according to established procedures (APHA 2005). BOD_5 was determined by using the WTW OxiTop® measuring system (Weilheim, Germany) following the Standard Method 5210D procedure. DOC was determined, after sample filtration through a $0.45 \mu\text{m}$ membrane, in a Shimadzu TOC-VCSN analyzer. Absorbance at 254 nm (UV_{254}) was measured in a spectrophotometer UV-vis, Lambda 20 (Perkin-Elmer) in order to evaluate its variation during the oxidation process and also calculate SUVA (specific UV absorbance) according to Method 415.3 (EPA 2005). Ammonium, nitrate, nitrite and other ions were determined by ionic chromatography using the equipment Advanced Compact IC Metrohm with Metrosep A Supp 4–250 columns.

Microscopic observations of the biofilm accumulated on the biomedia surface were made using an optical microscope (Optika) equipped with digital camera (Moticam 2300) and software (Motic Images Plus 2.0).

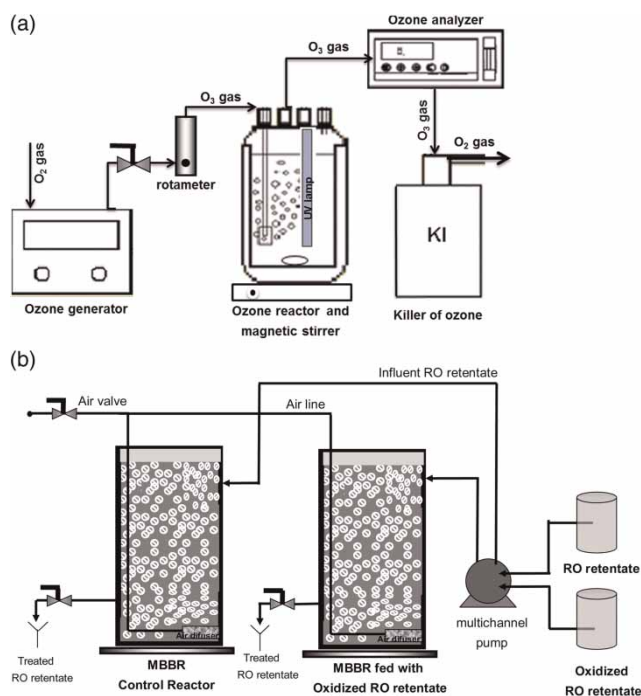


Figure 1 | Experimental set-up for RO retentate treatment: (a) set-up used in oxidation experiments (O_3 , O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$); (b) MBBR control reactor and MBBR fed with oxidized RO retentate.

RESULTS AND DISCUSSION

RO concentrate characteristics

The RO concentrate used during the experiments presented the composition shown in Table 1.

Some samples presented peaks of COD, DOC and, mainly, ammonium. The standard deviation values shown in Table 1 indicate that data scattering was high. Coefficients of variation of 25% were observed for DOC and COD and 36% for NH_4^+ .

Table 1 | RO retentate characteristics

DOC (mgC L ⁻¹)	24 ± 6.0	NH ₄ ⁺ (mgNH ₄ L ⁻¹)	127 ± 46	Cl ⁻ (mgCl L ⁻¹)	1,394 ± 54
COD (mgO ₂ L ⁻¹)	83 ± 20	Na ⁺ (mgNa L ⁻¹)	1,318 ± 103	NO ₃ ⁻ (mgNO ₃ L ⁻¹)	38 ± 3.4
Surfactants (mg L ⁻¹)	4.4 ± 3.8	K ⁺ (mgK L ⁻¹)	93 ± 2.0	NO ₂ ⁻ (mgNO ₂ L ⁻¹)	17 ± 0.4
UV ₂₅₄ (cm ⁻¹)	0.507 ± 0.016	Ca ²⁺ (mgCa L ⁻¹)	485 ± 21	PO ₄ ³⁻ (mgPO ₃ L ⁻¹)	39 ± 1.0
pH	7.0	Mg ²⁺ (mgMg L ⁻¹)	199 ± 13	SO ₄ ²⁻ (mgSO ₄ L ⁻¹)	1,144 ± 67

Organic matter removal in the oxidation experiments

All the tested oxidation processes were able to remove COD and DOC of the RO retentate, as shown in Table 2. In general, it is difficult to drop COD and DOC values when their initial values are already low (about 80 and 24 mg L⁻¹, respectively). Although the tested oxidation processes showed a satisfactory efficiency in terms of COD and DOC removal, they were more effective to drop the wastewater absorbance at 254 nm (63–74%), which indicates that the presence of double bound carbon compounds and aromatic substances was reduced, increasing the wastewater biodegradability. BOD determinations made before and after each oxidation process allowed calculation of the ratio BOD₅/COD. This ratio increased after oxidation. The BOD₅/COD was low (0.06) for the concentrate and increased to 0.15–0.26 after oxidation. The residual DOC of the treated concentrate was between 13 and 19 mgC L⁻¹. Although BOD and COD determinations can be influenced by salinity, in the present work the inorganic matrix was not changed after oxidation. Thus, if a possible effect of salinity occurred on both determinations, it was probably the same for the two wastewaters (retentate and oxidized retentate).

Lee *et al.* (2009) observed an increase of 1.8 to 3.5 times on RO retentate biodegradability after ozonation, using ozone doses of 3 to 10 mg L⁻¹ and reaction times of 10 and 20 min. These authors also verified that ozonation generated low molecular weight compounds (<1 kDa) from high molecular weight compounds. In the RO retentate,

compounds with molecular weight higher than 100 kDa corresponded to 80% of the organic matter. The SUVA, which corresponds to the ratio UV absorbance (254 nm)/DOC, decreased significantly from 2.1 L mg⁻¹ m⁻¹ for the retentate to values in the range of 0.8 to 1.1 L mg⁻¹ m⁻¹ for the oxidized retentate. As observed by Weishaar *et al.* (2003), SUVA is correlated with the organic matrix aromaticity. Thus, the pre-treatment with oxidants was able to oxidize a significant fraction of the aromatic compounds originally found in the retentate.

MBBR performance

Organic matter removal

The MBBR was fed with a stream presenting low organic matter content and, thus, was operated with a very low organic load (about 0.05 kgCOD m⁻³ d⁻¹). This was necessary due to the difficulty of treating biologically such diluted and complex wastewater. Operating under such conditions, with a dissolved oxygen level always above 7.0 mg L⁻¹, the MBBR was able to remove the residual organic matter to a larger extent, as shown in Table 3.

The results shown in Table 3 reveal that oxidation contributed significantly for organic matter removal. In particular, the combination of ozone, peroxide and UV (O₃/H₂O₂/UV) led to the highest removals of COD (36%) and DOC (53%), in contrast with the result attained in the control experiment, which presented lower removals (18%, COD and 14%, DOC).

Table 2 | COD, DOC, UV₂₅₄ removals and BOD₅/COD ratios attained after oxidation

Oxidation processes	COD removal (%)	DOC removal (%)	UV ₂₅₄ removal (%)	BOD ₅ / COD
O ₃	33 ± 6	15 ± 0.2	63 ± 1.8	0.15
O ₃ /UV	42 ± 5	29 ± 1.2	73 ± 1.2	0.18
O ₃ /H ₂ O ₂	48 ± 7	37 ± 1.9	67 ± 1.0	0.20
O ₃ /H ₂ O ₂ /UV	54 ± 5	44 ± 0.8	74 ± 0.7	0.26

Table 3 | COD and DOC removals attained in the MBBR

Processes	COD removal (%)	DOC removal (%)
Control	18 ± 8	14 ± 9
O ₃ + MBBR	27 ± 3	39 ± 0.2
O ₃ /UV + MBBR	29 ± 8	49 ± 1.2
O ₃ /H ₂ O ₂ + MBBR	25 ± 10	45 ± 1.9
O ₃ /H ₂ O ₂ /UV + MBBR	36 ± 10	53 ± 0.8

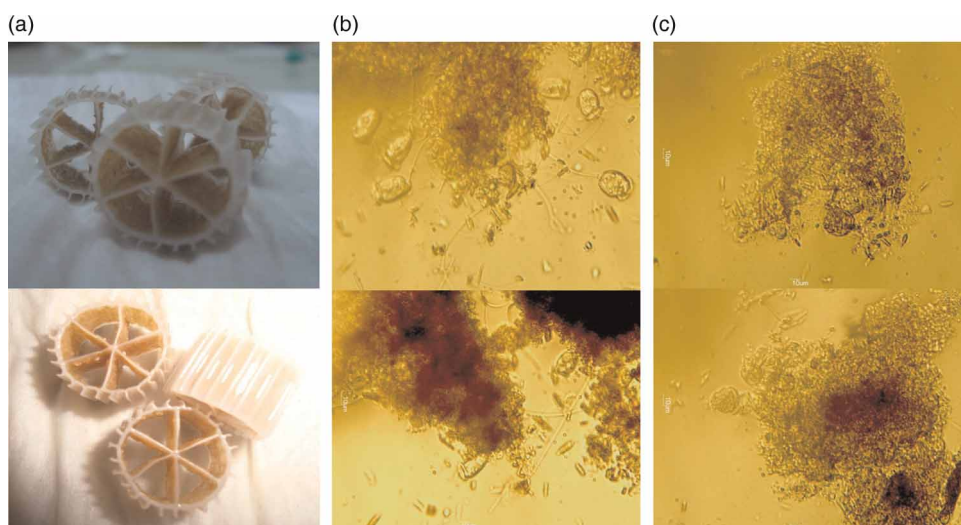


Figure 2 | Attached biomass characteristics: (a) thin biofilms on the biomedica surface; (b) protozoan and filaments observed in the control reactor; (c) dense agglomerates of biomass in the reactor fed with retentate previously oxidized.

Attached biomass characteristics

Attached biomass was carefully scraped from the carriers and used for volatile solids (VS) determination and also for microscopic observation. In general, carriers were recovered by thin biofilms (Figure 2(a)) presenting an important microbial diversity. A higher diversity was observed in the MBBR fed with the RO retentate (control reactor). In this case, protozoan and filaments were observed, as illustrated in Figure 2(b). Examination of the attached biomass collected from the MBBR operating with pre-oxidized wastewater revealed a lower diversity, in terms of protozoan population and the absence of filaments, as illustrated in Figure 2(c).

The attached biomass content, expressed as VS, was determined as $1,500 \text{ mg L}^{-1}$ (average) in the control reactor and 960 mg L^{-1} (average) in the MBBR operated with pre-oxidized wastewater. In terms of average specific COD removal the following results were obtained: $0.013\text{--}0.017 \text{ mgCOD}_{\text{removed}} \text{ mg}^{-1}\text{VS}$ (MBBR fed with oxidized retentate) and $0.010 \text{ mgCOD}_{\text{removed}} \text{ mg}^{-1}\text{VS}$ (MBBR control). The low values of specific COD removal are a consequence of the low organic load applied to the reactors and the relative recalcitrance of the pollutants found in the retentate.

The knowledge of microbiota involved in biofilms is important for operation and control of MBBR systems. The literature about biofilms grown on MBBRs is relatively scarce, especially, information about community composition, as pointed out by McQuarrie & Boltz (2011).

Ammonium removal

Removal of nitrogen was very high in the control reactor and moderate in the reactor fed with pre-oxidized wastewater (Table 4). It should be remarked that the control reactor was always fed with the same influent (RO retentate), whereas the MBBR was fed with different influents (produced by different oxidation processes). Thus, the control reactor had enough time to adapt and develop an effective nitrifying microbial community. In addition, the biodegradability increase promoted by retentate oxidation may have favored the implantation of heterotrophs in the reactor. As a consequence, these organisms competed for space and oxygen with nitrifiers and hindered nitrification. Another point to take into account is the influent ammonium concentration in the MBBR fed with pre-oxidized retentate. In general, it was lower than that

Table 4 | Ammonium removal results

Processes	Removal NH_4 (%)	Inlet NH_4 (mg L^{-1})	Residual NH_4 (mg L^{-1})	Produced NO_3 (mg L^{-1})
Control	91 ± 9	109 ± 50	12 ± 13	299 ± 11
O_3 + MBBR	64 ± 9	83 ± 10	29 ± 5	156 ± 3
O_3/UV + MBBR	66 ± 4	83 ± 8	26 ± 5	157 ± 29
$\text{O}_3/\text{H}_2\text{O}_2$ + MBBR	69 ± 7	72 ± 3	24 ± 3	134 ± 13
$\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ + MBBR	73 ± 4	69 ± 2	19 ± 3	145 ± 11

observed in the control reactor influent (109 mg L^{-1} , average). Even so, ammonium concentration in the reactor fed with pre-treated retentate was below 30 mg L^{-1} (average). This result suggests that hydraulic retention time should be increased to improve nitrification and assure a lower level of ammonium in the treated effluent.

Global performance

Analysing the global results obtained by the combined treatment process (oxidation + biological treatment in a MBBR), it can be verified that oxidation effectively contributed to reach higher levels of organic matter removal (COD and DOC), as shown in Figure 3, where the results of the control reactor were also presented just for comparison.

When the concentrate was pre-treated by oxidation, the final effluent DOC was comprised between 6 and 12 mg L^{-1} , whereas for the control reactor the effluent DOC was always in the range of 21 to 68 mg L^{-1} .

CONCLUSIONS

The RO retentate investigated in the present work had a relatively low and variable organic matter content ($24 \pm 6 \text{ mg L}^{-1}$, DOC and $83 \pm 20 \text{ mg L}^{-1}$, COD) and a relatively high and variable ammonium concentration ($127 \pm 46 \text{ mg L}^{-1}$). In addition, it presented moderate levels of chloride ($1,394 \pm 54 \text{ mg L}^{-1}$), Na^+ ($1,318 \pm 103 \text{ mg L}^{-1}$) and Ca^{2+} ($485 \pm 21 \text{ mg L}^{-1}$). Additionally, the retentate was considered not suitable for biological treatment, since its BOD_5/COD ratio was very low (0.06).

The retentate treatment by oxidation techniques was able to remove COD, DOC, and UV absorbance at 254 nm. As expected, the results obtained with ozonation

were improved when this technique was combined with UV radiation (O_3/UV) and peroxidation ($\text{O}_3/\text{H}_2\text{O}_2$). An additional improvement was observed when ozonation was combined with peroxidation and UV radiation ($\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$). Ozonation, mainly when combined with radiation and/or peroxidation, promoted oxidation of aromatic compounds and other substances originally found in the retentate. As a consequence, SUVA decreased significantly from 2.1 to $0.8\text{--}1.1 \text{ L mg}^{-1} \text{ m}^{-1}$, indicating a drop on the organic matrix aromaticity and biodegradability was increased, as expressed by the augmentation of the ratio BOD_5/COD from 0.06 (retentate) to $0.15\text{--}0.26$ (oxidized retentate).

Biological treatment of the retentate in a MBBR (control reactor) led to low removals of COD and DOC, respectively, 18 and 14%. When the MBBR was fed with pre-oxidized retentate, the removal efficiencies increased, attaining 36 and 53%, COD and DOC, respectively, for the retentate treated by $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$. However, ammonium removal was more effective in the control reactor (91%) than in the reactor fed with retentate treated by $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ (73%). Less time for nitrifiers adaptation and more favorable conditions for heterotroph growth, probably, contributed to hinder nitrification in that reactor.

Oxidation of the retentate contributed to obtain good results in terms of organic matter removal and reduction of organic matter aromaticity. The effluent of the combined process (oxidation + MBBR) presented low DOC levels, in the range of 6 to 12 mgC L^{-1} .

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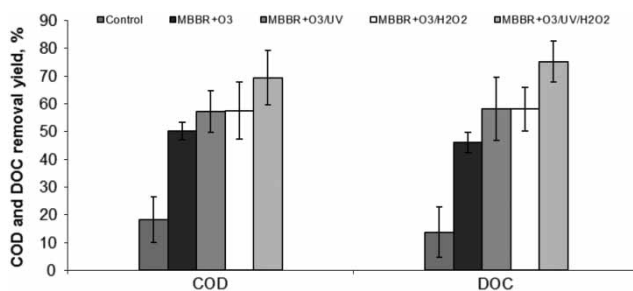


Figure 3 | COD and DOC removals attained in the MBBR control reactor and in the combined experiments (oxidation processes + MBBR).

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