

1 **Assessing the application of advanced oxidation processes, and their combination**
2 **with biological treatment, to effluents from pulp and paper industry**

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1 **Abstract**

2 The closure of water circuits within pulp and paper mills has resulted in a higher
3 contamination load of the final mill effluent, which must consequently be further treated
4 in many cases to meet the standards imposed by the legislation in force. Different
5 treatment strategies based on advanced oxidation processes (ozonation and TiO₂-
6 photocatalysis), and their combination with biological treatment (MBR), are herein
7 assessed for effluents of a recycled paper mill and a kraft pulp mill. Ozone treatment
8 achieved the highest efficiency of all. The consumption of 2.4 gO₃·L⁻¹ resulted in about
9 a 60% COD reduction treating the effluent from the kraft pulp mill at an initial pH=7;
10 although it only reached about a 35% COD removal for the effluent of the recycled
11 paper mill. Otherwise, photocatalysis achieved about a 20-30% reduction of the COD
12 for both types of effluent. In addition, the effluent from the recycled paper mill showed
13 a higher biodegradability, so combinations of these AOPs with biological treatment
14 were tested. As a result, photocatalysis did not report any significant COD reduction
15 improvement whether being performed as pre- or post-treatment of the biological
16 process; whereas the use of ozonation as post-biological treatment enhanced COD
17 removal a further 10%, summing up a total 90% reduction of the COD for the combined
18 treatment, as well as it also supposed an increase of the presence of volatile fatty acids,
19 which might ultimately enable the resultant wastewater to be recirculated back to further
20 biological treatment.

21

22 *Keywords:* Advanced oxidation processes; photocatalysis; ozonation; membrane
23 bioreactor; pulp and paper industry effluent.

24

1 **1. Introduction**

2 Despite the great efforts made by the paper industry to close its water circuits, it still
3 remains the second largest sector demanding water use [1]. Therefore, further
4 challenges should still be faced up in order to keep meeting current standards related to
5 the quantity and quality of discharged wastewater [2], and developing innovative
6 technologies for reusing and/or recycling wastewater within the process in order to
7 minimize the environmental impact of pulp and paper mills. Totally closing water
8 circuits using current available technologies may lead to significant trouble in the
9 process, as well as other problems related to water quality requirements. Therefore, new
10 treatment strategies should aim to remove biodegradable high molecular weight (HMW)
11 organic compounds, as well as low molecular weight (LMW) recalcitrant organic matter
12 [3].

13 In particular, new trends are focussed on incorporating alternative treatment
14 types like advanced oxidation processes (AOPs), which may be able to remove
15 recalcitrant compounds [4, 5]. In fact, AOPs have already been applied to industrial
16 wastewater as a polishing step integrated with conventional chemical and/or biological
17 processes in order to increase overall treatment efficiency [4, 6]. Furthermore, the
18 application of AOPs to pulp and paper mill effluents might only be economically
19 attractive in combination to other wastewater treatment type [7], particularly
20 considering they usually imply a high demand of energy, or an excessive reagents
21 consumption [8].

22 Moreover, the use of AOPs within pulp and paper mills should take into account
23 the influence of wastewater composition on its potential treatment. Pulp industry
24 effluents, such as those out-flowing from wood chemical pulping processes, generate

1 more than a 40% low biodegradable organics within the total organic matter content
2 present in the final effluent [9]. On the other hand, effluents from paper mills using
3 recovered paper as raw material are rather characterized by the presence of
4 biodegradable starch-related products than by their content of lignin compounds [10]. In
5 addition, it is also important to consider the efficiency of the process itself and the
6 development of adequate protocols for using these processes in mills with a high degree
7 of circuits closure [11]; as well as take into good account its economical assessment.

8 Ozonating wastewater from pulp and paper mills has been previously reported to
9 remove colour very easily because its main responsible is the presence of lignin
10 compounds, which double and triple bonds were easily oxidized by ozone [5, 12]. In
11 addition, ozonation has also been reported to increase the biodegradability of effluents
12 from pulp and paper mills, mainly because of the degradation of toxic compounds, and
13 the promoted changes in the molecular weight fractions (from HMW to LMW) [1, 13].

14 Complementarily, the application of TiO₂-photocatalytic treatment within the
15 pulp and paper industry has previously been reported to show an efficient reduction of
16 colour and dissolved organic carbon when heterogeneous TiO₂-photocatalytic processes
17 have been applied to different types of effluents and lignin-containing solutions; as well
18 as a rapid decrease of their toxicity and biodegradability improvement have also been
19 addressed [14-17].

20 In short, ozonation and photocatalysis have not usually been considered as
21 feasible treatments to be used standalone because of the large amounts of chemicals and
22 energy that they require for its proper performance; but their combination with
23 biological processes may increase the overall treatment efficiency [3, 18], therefore
24 enhancing their viability.

1 Among available biological technologies, membrane biological reactors (MBR)
2 involve important advantages over other more conventional biological processes,
3 namely: a superior resulting effluent quality, higher control of solids and hydraulic
4 retention time, and smaller installation volume and footprint [19]. As a consequence,
5 they have previously been considered for enhancing sustainable water reuse within
6 paper mills [20]; moreover if a final reverse osmosis step is required [21].

7 A comparative essay is herewith reported considering two very different
8 effluents from pulp and paper industry (a kraft pulp mill, and a 100% recycled paper
9 mill effluents) in order to assess the influence of wastewater composition on AOPs
10 efficiency. In addition, combination alternatives of AOPs and MBR technologies are
11 also reported for the recycled paper mill effluent.

12

13 **2. Materials and methods**

14 *2.1. Material and analytical methods*

15 All used chemicals were of analytical grade and supplied by PANREAC S.A.
16 (Barcelona, Spain). The catalyst AEROXIDE® TiO₂ P 25 was supplied by Evonik
17 Degussa GmbH (Essen, Germany). All solutions were prepared in ultrapure water and
18 preserved in the dark.

19 The final effluents from a recycled paper mill and a kraft pulp mill were sampled
20 and preserved in polyethylene bottles protected from light inside a refrigerator at 4 ±
21 1°C until use. Their main analytical characteristics are shown in Table 1. Sample
22 preservation and all analyses were performed according to the standard methods for the
23 examination of water and wastewaters [22].

1 In particular, chemical oxygen demand (COD), and soluble chemical oxygen
2 demand (sCOD) were measured by the colorimetric method at 600 nm, using an
3 Aquamate spectrophotometer (Thermo Scientific AQA 091801, Waltham, USA) after
4 filtrating the samples through 0.45 μm . pH was adjusted adding 1M H_2SO_4 or 1N
5 NaOH when necessary. Colour was estimated using the Pt-Co method, turbidity was
6 determined by the nephelometric method, and volatile fatty acids (VFA) content was
7 measured by the colorimetric method described by Harwood and Huyser [23].

8

9 *2.2. Experimental procedures*

10 All the following treatments (ozonation, UV or solar TiO_2 -photocatalysis,
11 biodegradability test, and MBR) were applied stand-alone, or in combination (ozonation
12 or solar photocatalysis + biodegradability test, MBR + ozonation or solar
13 photocatalysis) to effluents from the pulp and paper industry taking into account their
14 main characteristics.

15

16 *2.2.1. Ozonation*

17 Ozonation trials were performed in a glass jacketed cylindrical bubble reactor (height =
18 1 m, diameter = 5 cm) with a continuous feed of ozone gas ($4.0 \text{ L}\cdot\text{min}^{-1}$) produced from
19 ordinary grade air passed through polycarbonate filters, and subsequently enriched with
20 oxygen. The ozone feeding system consisted of an ozone generator (Model 6020, Rilize,
21 Gijón, Spain), and a flow controller Bronkhorst® (Model F-201AV, Ruurlo, The
22 Netherlands). As a result, $3 \text{ g}\cdot\text{h}^{-1}$ of ozone were continuously fed into the reactor. In
23 order to determine the real ozone consumption inside the reactor, in-flow and out-flow
24 ozone concentrations were measured using two on-line ozone analyzers (Model 964C,

1 BMT Messtechnik GMBH, Berlin, Germany). Therefore, the real specific ozone dose
2 that was consumed in the reactor, which also depends on the nature and concentrations
3 of the compounds being generated along the process, could be measured. Unconsumed
4 ozone was sent to a catalytic ozone destructor.

5 In addition, a peristaltic pump (Masterflex® Console Drive, Cole-Parmer
6 Instrument Company, Illinois, USA) was used to recirculate the solution being treated
7 (1.5 L) through the reactor; and probes for pH, redox potential and dissolved oxygen
8 (ProODO, YSI Inc., Ohio, USA) were used for controlling the process on-line.

9 Temperature was kept at 25°C using a thermostatic bath (Model FL300,
10 JULABO Labortechnik GmbH, Seelbach, Germany) that was aided by the reactor's
11 glass jacket itself; and the initial pH of the effluent was set before supplying ozone to
12 the sample. A basic value (pH=12, supposed to potentially produce better treatment
13 results [24]) and the neutral one (pH=7, which is closer to the natural values of the
14 effluents; Table 1) were selected to perform this trials. Achieving good results at a
15 lower operational cost avoiding initial pH adjustment would be of valuable application
16 interest. Each ozonation trial was performed for 5 hours. Samples were taken every hour
17 for COD, colour, and VFA determination.

18

19 2.2.2. *Photocatalysis*

20 The photocatalytic process was performed in a reactor with a 450-W high-pressure
21 mercury immersion lamp from ACE-glass (Vineland, USA). The total radiated power in
22 the visible and UV regions was 159.4 W (47.5% and 52.5%, respectively). Major
23 emission bands (>3%) were located at 578.0 nm (12.5%), 546.1 nm (15.4%), 435.8 nm
24 (12.7%), 404.5 nm (6.9%), 366.0 nm (16.1%), 313.0 nm (8.3%), 302.5 nm (4.5%), and

1 253.7 nm (3.6%). A total photon flux of $1.1 \cdot 10^{20}$ photon \cdot s $^{-1}$ was calculated, as described
2 in Liang *et al.* [25], to flow inside the photochemical reactor.

3 Light intensity was recorded using a radiometer (UV-Elektronik, UV-VIS
4 Radiometer RM-21, Ettlingen, Germany), resulting in $186 \text{ mW}\cdot\text{cm}^{-2}$ between 315 and
5 400 nm at the mid-height of the UV-lamp, and at 1.5 cm from the light source, which
6 was the actual distance to the sample. The lamp was enclosed inside a quartz glass
7 vessel through which water was circulated to reduce the excessive heat generated during
8 UV irradiation, and it was vertically located in the centre of the reactor. The entire
9 assembly was kept inside a photochemical safety cabinet.

10 Aeroxide® TiO₂ P25 (Evonik Degussa GmbH, Essen, Germany) was used as the
11 catalyst of the reaction. The main properties of this product are: BET surface area = 50
12 m²/g, pore volume = 0.25 m³/g, and mean particle size of ca. 30 nm. The concentration
13 of TiO₂ and reaction time were optimized at the same two different initial pH values (7
14 and 12) justified for ozonation, and at a constant temperature of 25°C. pH, redox
15 potential, and dissolved oxygen were measured on-line during treatment using
16 appropriate probes (ProODO YSI Inc., Ohio, USA). Each photocatalytic trial was
17 performed for 5 hours. Samples were taken every hour for COD, colour, and VFA
18 determination.

19

20 2.2.3. Solar photocatalysis

21 Solar photocatalysis trials were carried out in a solar simulator equipped with a Xenon
22 lamp (300 W) supplied by Newport (Irvine, USA). Intensity and power could be pre-
23 selected for each experimental run, and a filter was used to correct the illuminator out to
24 obtain a solar spectrum under ideal conditions (ASTM E490-73a). The total radiated

1 power in the visible and UV regions was 106.5 W (51.7% and 48.3%, respectively).
2 Major emission bands (>3%) were located at 578.0 nm (17.4%), 546.1 nm (16%), 435.8
3 nm (10.9%), 404.5 nm (7.5%), 366.0 nm (6.3%), 334.1 nm (4.4%), 313.0 nm (3.9%),
4 302.5 nm (3.7%), 296.7 nm (3.6%), 289.4 nm (3.2%), and 280.4 nm (3.0%). A total
5 photon flux of $6.8 \cdot 10^{19}$ photon \cdot s $^{-1}$ was calculated, as described in Liang *et al.* [25], to
6 flow inside the photochemical reactor.

7 Light intensity was recorded using a radiometer (UV-Elektronik, UV-VIS
8 Radiometer RM-21, Ettlingen, Germany), resulting in 98.9 mW \cdot cm $^{-2}$ between 315 and
9 400 nm at the mid-surface of the Xe lamp, and at 12 cm from the light source, which
10 was the real distance to the sample.

11 The concentration of TiO $_2$ and reaction time were optimized at an initial pH=7,
12 as it already produced better results in the previously performed photocatalytic trials,
13 and T=25°C. pH, redox potential and dissolved oxygen were on-line measured along
14 treatment using adequate probes (ProODO YSI Inc., Ohio, USA) during the trials.

15

16 2.2.4. Biodegradability test

17 Zahn-Wellens/EMPA Test [26] was used to determine the inherent biodegradability of
18 effluents, for which 7-days-old activated sludge was collected from the wastewater
19 treatment plant located at the recycled paper mill. This biodegradation process was
20 monitored measuring the COD in filtered subsamples subtracted along the reaction until
21 its maximum reduction was achieved.

22 The functional power of the activated sludge was checked running a parallel test
23 using ethylene glycol as reference substance. Its biodegradability at least reached a 70%
24 COD reduction within the first 14 days of incubation. The ratio of removed COD to its

1 initial value, corrected considering control results, provides the percentage of
2 biodegradation that was achieved along the process.

3

4 2.2.5. MBR treatment

5 The MBR pilot system that was used during combined treatment trials with AOPs was a
6 ZeeWeed-10 from Zenon (GE; Conneticut, USA) with an outside/in ultrafiltration
7 hollow fibre membrane. The membrane module that was used had a mean pore size of
8 0.04 μm , and an effective filtration area of 0.93 m^2 ; and the system assembled two
9 process tanks summing up a total effective volume of 70 L. Wastewater was pumped
10 through the membrane by developing a negative pressure (vacuum) across using a gear
11 pump (Verder VGS060.17, maximum 60 $\text{L}\cdot\text{h}^{-1}$) that was regulated by a frequency
12 controller.

13 The MBR started up with 70 L of returned activated sludge collected at the
14 wastewater treatment plant installed at the recycled paper mill, and it was fed with
15 effluent from this mill after being subjected to sedimentation. In terms of operation, the
16 process consisted on 300 s of direct filtration, and 20 s of backwash. Solids were
17 removed out via direct filtration.

18 Sludge drainage was initially set at 0.4 $\text{L}\cdot\text{h}^{-1}$ in order to regulate biomass content
19 inside the MBR, allowing its growth until a target value of solids concentration was
20 reached. Subsequently, values between 0.4 and 0.9 $\text{L}\cdot\text{h}^{-1}$ were set to regulate the
21 concentration of solids inside the tanks. The biomass inside the MBR was controlled
22 measuring mixed liquor volatile suspended solids (MLVSS), which average value
23 resulted 5.92 $\text{g}\cdot\text{L}^{-1}$. Average sludge age was 16 days at 24 hours of hydraulic retention
24 time (HRT), and 5 days at 8 hours HRT. Total suspended solids (TSS), turbidity, COD,

1 VFA, MLSS (mixed liquor suspended solids), MLVSS, total nitrogen, and phosphate
2 contents were measured twice a week during the trials.

3

4 **3. Results and discussion**

5 *3.1. Comparative assessment of the advanced oxidation treatment of effluents from pulp*
6 *and paper industry*

7 *3.1.1. Ozone treatment*

8 The required ozone dose for an optimal treatment and the efficiency of the process
9 therefore, were dependent on the concentration of ozone in the inlet gas, reaction time
10 [27], and the nature and concentrations of organic and inorganic compounds in the
11 treated effluent. In short, the evolution of ozone consumption resulted different during
12 treatment (Figures 1 and 2) because of the continuous reaction of ozone with the
13 changing content of organic and inorganic compounds present in the solution. As a
14 result, the real specific ozone dose that was consumed in the reactor reached 3.6 mg O₃
15 per mg of removed COD for the effluent from the recycled paper mill, and 2.38 mg O₃
16 per mg of removed COD for the effluent from the kraft pulp mill, when 2.4 g·L⁻¹ of
17 ozone were consumed at an initial pH=7; as it can be calculated from Figures 1 and 2.

18 In fact, the ozone treatment of the effluent from the recycled paper mill showed
19 a lower reduction of the COD (Figures 1 and 2), which may be attributed to its higher
20 concentration of compounds that are difficult to oxidize (VFA, mainly); and a higher
21 amount of bicarbonate (Table 1), which has been previously reported to produce certain
22 scavenging effect [28]. In short, aliphatic organic compounds have previously widely
23 been described to be difficult to oxidize by AOPs [29, 30], resulting in an increase of
24 the specific consumption of ozone, and the consequent decrease of the efficiency of the

1 treatment. As a result, about a 60% reduction of the COD was achieved ozonating the
2 effluent of the kraft pulp mill at an initial pH=7 (2.4 g·L⁻¹ of consumed ozone; Figure
3 2); whereas this treatment only reached about a 35% COD removal for the effluent of
4 the recycled paper mill (Figure 1).

5 Although several authors have reported a higher effectiveness of ozone
6 treatment at basic pH values [1, 5, 24], because the formation of hydroxyl radicals is
7 expected to be more efficient [3, 31], the ozonation of the recycled paper mill effluent
8 only showed some non-significant differences ($p < 0.05$) between the achieved COD
9 removals at an initial pH=7 and pH=12 (Figure 1). On the other hand, the application of
10 this treatment to the effluent from the kraft pulp mill resulted in a significant higher
11 COD reduction at an initial pH=7 than at pH=12 (Figure 2). These results may be the
12 consequence of the usual high alkalinity figures that characterise effluents from pulp
13 and paper mills (Table 1), which might have scavenged hydroxyl radicals at high pH
14 values; whereas it may otherwise be rather beneficial at a lower pH value buffering the
15 process [28].

16 In addition, a higher ozone dose than the strictly being devoted to oxidation
17 might have been required at pH=12 because higher pH values may also accelerate the
18 decomposition of ozone; so its specific overall consumption per unit of removed COD
19 was therefore higher than the expected to just perform the oxidation treatment [28]. In
20 conclusion, whatever particular side effects were affecting the process, results showed
21 that these effluents would be suitable for their (almost) best oxidation treatment at their
22 usual neutral pH value; therefore avoiding the cost of pH control operations at industrial
23 scale.

1 The ozone treatment of these effluents was performed through consecutive
2 oxidation stages (Figures 1-2) involving different ozone dosage consumptions
3 depending on the organic load of the solution, and the initial pH value of the effluent. In
4 short, two main reaction stages do really consecutively happen along the process: (1) a
5 first one where easily oxidizable compounds were mainly degraded; and (2) a second
6 one where oxi-recalcitrant by-products (VFA mainly [32, 33]) that are formed along the
7 process are attempted to be further oxidized [2, 12]. As a result, a steepest removal of
8 the COD was shown at the beginning of the process due to the effective degradation of
9 oxidable products ($0.5-1.0 \text{ g}\cdot\text{L}^{-1} \text{ O}_3$, depending on the type of effluent; Figures 1-2);
10 whereas reaction efficiency thereafter turned to progress smoothly as the content of oxi-
11 recalcitrant by-products increased in the solution even though ozone dosage
12 progressively rose as well. In fact, the limitation of TOC abatement is one of the results
13 of this increasing accumulation of oxi-recalcitrant compounds [34]; although they are
14 generally characterized for being highly biodegradable, which enables the possibility of
15 adding a biological treatment stage afterwards.

16

17 *3.1.2. Photocatalysis*

18 The maximum reduction of the COD that was achieved treating the same pulp and
19 paper effluents by photocatalysis resulted lower than the figures just reported for their
20 ozonation (Figures 1-2) in all the tested cases, whether using UV light ($\approx 20-25\%$;
21 Figure 3), or assisting the process with a solar simulator ($\approx 25-30\%$; Figure 4); just as it
22 would have been expected from previously reported trials [1, 2, 35].

23 Although degradation results showed the same tendency whichever light source
24 was used, the reduction of the COD resulted slightly higher ($<5\%$) when the solar

1 simulator was used, particularly at the higher tested TiO₂ concentration level (10 g
2 TiO₂·L⁻¹; Figures 3-4). This particular might ultimately be explained in terms of
3 differential characteristics of the incident light, and other properties of the used reactors
4 that might have somehow changed the distribution and efficiency of the suspended
5 catalyst. In this case, using the sun as light source would at least result in the reduction
6 of the energetic cost of the treatment without meaning any efficiency loss.

7 In addition, similar non-significant slight COD removal differences were also
8 found between the photocatalytic treatments of both tested effluents, resulting that
9 higher treatment efficiency was achieved for the effluent from the kraft pulp mill; as it
10 has also been reported for its ozone treatment, and may also be partially explained by
11 the higher content of oxi-recalcitrant aliphatic organic compounds that is present in the
12 effluent sampled at the paper mill (e.g. VFA content in Table 1).

13 The efficiency of these photocatalytic processes was much influenced by the
14 dosage of TiO₂ (Figures 3-4), resulting in a higher degradation of organics when the
15 TiO₂ concentration was also higher (up to 10 g TiO₂·L⁻¹) regardless the light source
16 (UV or solar) and initial pH value (7 or 12) that were used. These results are in
17 accordance with those reported in Chang *et al.* [16] for a similar treatment of lignin
18 powder. A concentration of TiO₂ higher than 10 g·L⁻¹ was not considered in the trials
19 because it has previously been reported to cause a shadow effect interfering with the
20 transmission of light, so the generation of electron-hole pairs cannot effectively occur
21 under such excessive catalyst content [15, 16].

22 Although several authors have reported good reductions of organic compounds
23 performing photocatalytic treatment at both neutral and basic initial pH values [15, 16,
24 36], the fact is that removal of the COD resulted higher when UV-photocatalysis was

1 performed at pH=7 for both types of effluents (Figure 3). This may partially have been
2 caused by the more or less strong competition that anions, cations, and some neutral
3 molecules exert against organic contaminants for the reactive sites on the surface of
4 TiO₂ particles; thus decreasing the overall process efficiency whether being performed
5 at basic or acid pH values. In short, the reaction rate would have been slowed down by
6 anion adsorption on the surface of the positively charged catalyst under acid conditions;
7 whereas catalytic particles negatively charge, and the presence of cations might
8 therefore have moderated the reaction rate, under basic pH values [37].

9 10 *3.2. The combination of AOPs and biological treatment to an effluent from a recycled* 11 *paper mill*

12 *3.2.1. MBR start-up*

13 There were initially 4 g·L⁻¹ of volatile suspended solids in the MBR, which were
14 increased to average 5-6 g·L⁻¹ along the biological treatment performance. A higher
15 concentration of 8 g·L⁻¹ was also tested, but treatment efficiency was not significantly
16 enhanced, and an excessive membrane fouling was generated. Total suspended solids
17 averaged about 2 g·L⁻¹ higher values than the content of volatile suspended solids.

18 The COD values measured in the permeate flowing out the MBR were very
19 stable during all the process despite the variability of inlet wastewater quality (Figure
20 5). The average sCOD value of this permeate was 250 mgO₂·L⁻¹ when HRT was kept
21 for 24 h [feed/microorganisms (F/M) ≈0.44 Kg COD/Kg MLSS·day], and 500 mgO₂·L⁻¹
22 when HRT was also evaluated at 8 hours [(F/M) ≈1.21 Kg COD/Kg MLSS·day],
23 which is close to the actual value that is used in this and other similar mills.

1 Sludge age resulted 16 days, and sludge retention time (SRT) was about 7.3 days
2 for a 24 h HRT. This short SRT favoured the enrichment of the sludge with bacterial
3 species of high growth rate [38]. Particularly, a similar short SRT has also previously
4 been reported addressing that the COD of the effluent was not influenced by changing
5 SRT [38, 39]. In addition, it is also well-known that a longer SRT favours the growth
6 .of specialized bacteria enhancing the breakdown of large macromolecules [40], the
7 sludge of the MBR was previously acclimated to the wastewater to be treated in this
8 particular case, and a longer SRT was not therefore finally required for an efficient
9 biological treatment. In fact, the MBR effectively worked removing all biodegradable
10 COD; therefore producing an appropriate effluent to be tested for an oxidation post-
11 treatment.

12 BOD₅ values of permeate were often lower than 10 mgO₂·L⁻¹ during the first
13 stage of HRT=24 h; and they resulted even slightly higher for HRT=8 h. A total to an
14 almost complete degradation of biodegradable organic matter was finally achieved by
15 this treatment (Figure 5). In addition, turbidity was in average reduced from 300 to 2
16 NTU; whereas suspended solids were totally removed.

17 The membrane always showed a good behaviour during treatment; although the
18 optimization of this membrane treatment is not herewith reported because it would not
19 result representative for industrial application. In fact, it would be necessary to perform
20 pilot trials with membrane systems of similar characteristics than those that will be
21 applied at industrial scale, which generally use a small number of full-scale membranes
22 modules, in order to obtain scalable results of this type of MBR system [41].

23

24 *3.2.2. The combination of AOPs with biological post-oxidation treatment*

1 In short, the oxidation treatment of the effluent from a recycled paper mill showed
2 worse results than the effluent from the kraft pulp mill; but biodegradability results were
3 much higher ($\approx 75\%$). Therefore, the combination of AOPs with a biological post-
4 treatment was also tested in order to assess whether COD reduction efficiency might be
5 improved for the effluent from the recycled paper mill, considering the expected
6 capacity of AOPs to increase the biodegradability of this type of effluents [3, 5, 13], and
7 that it would imply a lower overall treatment cost. Solar radiation was the only
8 photocatalytic treatment being assessed because it showed similar to even better results
9 than UV-light, and its application would also be much cheaper.

10 A balance between the potential cost of treatment alternatives and their
11 efficiency was considered when selecting the reaction conditions of each AOP +
12 biological combination treatment. Considering the above reported results for standalone
13 AOPs, the following best treatment conditions were tested: (a) 1 and 0.5 $\text{g}\cdot\text{L}^{-1}$ of ozone
14 at $\text{pH}=7$ for ozonation; and (b) 5 and 10 $\text{g}\cdot\text{L}^{-1}$ of TiO_2 along 0.5 and 1.0 h of solar
15 photocatalytic treatment at $\text{pH}=7$ as well. In addition, the effluent's threshold of
16 biodegradability was determined before performing oxidation in order to properly
17 compare it with the biodegradability results of the already oxidized effluent (Figure 6).

18 In summary, COD reduction did not result strongly improved after any previous
19 oxidation process; although 1 $\text{g}\cdot\text{L}^{-1}$ ozone treatment and 5 $\text{g}\cdot\text{L}^{-1}$ photocatalytic
20 process slightly enhanced biodegradability ($\approx 5\%$; Figure 6). On the other hand, 10 g
21 $\text{TiO}_2\cdot\text{L}^{-1}$ solar photocatalysis did not particularly result in higher post-biological COD
22 reduction probably because a greater amount of biodegradable organic matter was
23 already consumed during the oxidative process, as addressed by the better efficiency
24 figures that were achieved when this treatment was performed standalone (Figure 4).

1

2 *3.2.3. The application of AOPs as post-MBR biological treatment*

3 Finally, the effluent from the recycled paper mill was firstly treated in the MBR, and the
4 generated permeate was thereafter treated by ozonation and solar photocatalysis in order
5 to assess the overall efficiency of this treatment strategy as well. Those reaction
6 conditions addressing better biodegradability results (Figure 6) were also applied in
7 these trials, that is: (a) $1 \text{ g O}_3 \cdot \text{L}^{-1}$ for ozonation, and (b) $5 \text{ g TiO}_2 \cdot \text{L}^{-1}$ for a 30 min solar
8 photocatalysis; both performed at $\text{pH}=7$.

9 The standalone MBR treatment reached an 80% COD reduction with an almost
10 total consumption of organic fatty acids (VFA), and a reduction of colour higher than
11 the 40% (Figure 7). The 20% remaining COD in its permeate was mainly made up of
12 bio-recalcitrant COD, thus susceptible of being further treated by AOPs. In fact, the
13 ozone oxidation of this permeate achieved a further 40% reduction of the remaining
14 COD (Figure 7); thus enhancing the overall COD removal a significant additional 10%
15 approx. (Figure 8). On the other hand, solar photocatalysis only achieved an extra 10%
16 removal of the COD outlasting biological treatment (Figure 7). In addition, ozone was
17 able to almost completely remove persisting colour in the permeate ($\approx 95\%$); as well as it
18 produced an increase of VFA content, thus enabling the recirculation of the ozonised
19 permeate back to the MBR in order to further increase treatment efficiency.

20 In summary, although all tested configurations combining biological and
21 advanced oxidation processes resulted in the enhancement of the overall reduction of
22 the COD, the highest COD removal was achieved treating the effluent from the recycled
23 paper mill by a biological stage followed by the ozone treatment of the generated
24 permeate (Figure 8). In short, the remaining bio-recalcitrant fraction could be more

1 efficiently ozonised when the initial biodegradable load of this effluent was previously
2 biologically removed. Nevertheless, the biological process was able to efficiently
3 remove most of its contaminant load; so ozone post-treatment would only be required
4 when very stringent discharge requirements, in both quantity and/or quality terms, may
5 be imposed.

6

7 **4. Conclusions**

8 The treatment of effluents from pulp and paper mills was highly influenced by the
9 composition of each type of wastewater, resulting that effluents from recycled paper
10 mills were more biodegradable than those generated in kraft pulp mills. In consequence,
11 better results were obtained when the kraft pulp mill effluent was treated by AOPs.

12 Ozonation achieved a higher COD reduction than photocatalysis, that was about
13 a 35% for the effluent from a recycled paper mill, and about a 60% for the effluent
14 sampled at a kraft pulp mill at an initial pH=7.

15 Photocatalysis achieved lower COD removals treating both effluents under the
16 best designed reaction conditions; namely, about a 25% for the effluent from the
17 recycled paper mill and almost the 30% for the effluent from the kraft pulp mill.

18 The effluent from the recycled paper mill was successfully treated in a
19 membrane bioreactor thanks to its high biodegradable nature; thus achieving a very high
20 reduction of the COD (80%).

21 The combination an AOP pre-treatment with an MBR biological process did not
22 result in a significant higher overall efficiency.

1 In addition, the combination of an MBR biological stage with a TiO₂-
2 photocatalysis post-treatment only reported a slight improvement of a further 10%
3 reduction of the COD.

4 On the other hand, the combination of this biological process with an ozonation
5 post-treatment achieved very good removals of COD and colour (approx. 90% and 95%,
6 respectively); as well as it increased the biodegradability of the final effluent, therefore
7 allowing the potential successful recirculation of the resultant wastewater back to
8 receive further MBR treatment.

9

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16

17 **References**

- 18 [1] A.M. Amat, A. Arques, M.A. Miranda, F. López, Use of ozone and/or UV in the
19 treatment of effluents from board paper industry, *Chemosphere* 60 (2005) 1111-1117.
20 [2] V. Fontanier, S. Baig, J. Albet, J. Molinier, Comparison of conventional and
21 catalytic ozonation for the treatment of pulp mill wastewater, *Environ. Eng. Sci.* 22
22 (2005) 127-137.

- 1 [3] L. Bijan, M. Mohseni, Integrated ozone and biotreatment of pulp mill effluent and
2 changes in biodegradability and molecular weight distribution of organic compounds,
3 *Water Res.* 39 (2005) 3763-3772.
- 4 [4] I.A. Balcioglu, I.A. Alaton, M. Ötker, R. Bahar, N. Bakar, M. Ikiz, Application of
5 advanced oxidation processes to different industrial wastewaters, *J. Environ. Sci.*
6 *Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* A38 (2003) 1587-1596.
- 7 [5] L. Bijan, M. Mohseni, Using ozone to reduce recalcitrant compounds and to enhance
8 biodegradability of pulp and paper effluents, *Water Sci Technol.* 50 (2004) 173-182.
- 9 [6] A.B.C. Alvares, C. Diaper, S.A. Parsons, Partial oxidation by ozone to remove
10 recalcitrance from wastewaters – A review, *Environ. Technol.* 22 (2001) 409-427.
- 11 [7] V. Sarria, S. Parra, N. Adler, P. Péringier, N. Benitez, C. Pulgarin, Recent
12 developments in the coupling of photoassisted and aerobic biological processes for the
13 treatment of biorecalcitrant compounds, *Catal. Today* 76 (2002) 301-315.
- 14 [8] R. Bauer, H. Fallmann, The photo-Fenton oxidation-A cheap and efficient
15 wastewater treatment method, *Res. Chem. Intermed.* 23 (1997) 341-354.
- 16 [9] O.B. Dahlman, A.K. Reimann, L.M. Stromberg, R.E. Morck, High-molecular-
17 weight effluent materials from modern ECF and TCF bleaching, *Tappi J.* 78 (1995) 99-
18 109.
- 19 [10] G. Thompson, J. Swain, M. Kay, C.F. Forster, The treatment of pulp and paper
20 mill effluent: a review, *Bioresour. Technol.* 77 (2001) 275-286.
- 21 [11] A.M. Amat, A. Arques, S. López, M.A. Miranda, Solar photo-catalysis to remove
22 paper mill wastewater pollutants, *Sol. Energy* 79 (2005) 393-401.

- 1 [12] A. Salokannel, J. Heikkinen, M. Kumpulainen, M. Sillanpää, J. Turunen, Tertiary
2 treatment of pulp and paper mill wastewaters by ozonation and O₃/H₂O₂ techniques,
3 *Paperi ja Puu-Paper and Timber* 89 (2007) 348-351.
- 4 [13] I.A. Balcioglu, E. Tarlan, C. Kivilcimdan, M.T. Saçan, Merits of ozonation and
5 catalytic ozonation pre-treatment in the algal treatment of pulp and paper mill effluents,
6 *J. Environ. Manage.* 85 (2007) 918-926.
- 7 [14] M.C. Yeber, J. Rodríguez, J. Freer, N. Durán, H.D. Mansilla, Photocatalytic
8 degradation of cellulose bleaching effluent by supported TiO₂ and ZnO, *Chemosphere*
9 41 (2000) 1193-1197.
- 10 [15] E.C. Catalkaya, F. Kargi, Advanced oxidation treatment of pulp mill effluent for
11 TOC and toxicity removals, *J. Environ. Manage.* 87 (2008) 396-404.
- 12 [16] C.N. Chang, Y.S. Ma, G.C. Fang, A.C. Chao, M.C. Tsai, H.F. Sung, Decolorizing
13 of lignin wastewaters using the photochemical UV/TiO₂ process, *Chemosphere* 56
14 (2004) 1011-1017.
- 15 [17] D. Hermosilla, N. Merayo, R. Ordoñez, A. Blanco, Optimization of conventional
16 Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis
17 retentate from a paper mill, *Waste Manage.* 32 (2012) 1236-1243.
- 18 [18] A.A. Morais, A.H. Mounteer, D.S.A. Silveira, Improvement of eucalyptus
19 bleached kraft pulp effluent treatment through combined ozone-biological treatment,
20 *Tappi J.* 7 (2008) 26-32.
- 21 [19] E. Dialynas, E. Diamadopoulos, Integration of a membrane bioreactor coupled with
22 reverse osmosis for advanced treatment of municipal wastewater, *Desalination* 238
23 (2008) 302-311.

- 1 [20] N.I. Galil, Y. Livinsky, Sustainable reclamation and reuse of industrial wastewater
2 including membrane bioreactor technologies: case studies, *Desalination* 202 (2007)
3 411-417.
- 4 [21] R. Ordoñez, D. Hermosilla, I. San Pío, A. Blanco, Replacement of fresh water use
5 by final effluent recovery in a highly optimized 100% recovered paper mill, *Water Sci.*
6 *Technol.* 62 (2010) 1694-1703.
- 7 [22] APHA, AWWA, WPCF (Eds.). Standard methods for the examination of water and
8 wastewater, Washington DC, 2005.
- 9 [23] J.E. Harwood, D.J. Huysen, Simplified automated volatile fatty acids analysis,
10 *Water Res.* 2 (1968) 631–636.
- 11 [24] R. Wang, C.L. Chen, J.S. Gratzl, Dechlorination and decolorization of chloro-
12 organics, in pulp bleach plant E-1 effluents, by advanced oxidation processes,
13 *Bioresour. Technol.* 94 (2004) 267-274.
- 14 [25] X. Liang, X. Zhu, E.C. Butler, Comparison of four advanced oxidation processes
15 for the removal of naphthenic acids from model oil sands process water, *J. Hazard.*
16 *Mater.* 190 (2011) 168-176.
- 17 [26] U. S. EPA. 712-C-98-084. Fate, Transport and Transformation Test Guidelines.
18 OPPTS 835.3200 Zahn-Wellens/EMPA Test, 1998.
- 19 [27] A.M. Amat, A. Arques, H. Beneyto, A. García, M.A. Miranda, S. Seguí,
20 Ozonisation coupled with biological degradation for treatment of phenolic pollutants: a
21 mechanistically based study, *Chemosphere* 53 (2003) 79-86.
- 22 [28] H. Barndöck, D. Hermosilla, L. Cortijo, C. Negro, A. Blanco, Assessing the effect
23 of inorganic anions on TiO₂-photocatalysis and ozone oxidation treatment efficiencies,
24 *J. Adv. Oxid. Technol.* 15 (2012) 125-132.

- 1 [29] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater
2 treatment I: oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004)
3 501-551.
- 4 [30] D. Hermosilla, M. Cortijo, C.P. Huang, The role of iron on the degradation and
5 mineralization of organic compounds using conventional Fenton and photo-Fenton
6 processes, *Chem. Eng. J.* 155 (2009) 637-646.
- 7 [31] W.H. Glaze, J.W. Kang, D.H. Chapin, *The Chemistry of Water-Treatment*
8 *Processes Involving Ozone, Hydrogen-Peroxide and Ultraviolet-Radiation*, *Ozone: Sci.*
9 *Eng.* 9 (1987) 335-352.
- 10 [32] T. Kreetachat, M. Damrongsri, V. Punsuwon, P. Vaithanomsat, C. Chiemchaisri,
11 C. Chomsurin, Effects of ozonation process on lignin-derived compounds in pulp and
12 paper mill effluents, *J. Hazard. Mater.* 142 (2007) 250-257.
- 13 [33] D. Hermosilla, M. Cortijo, C.P. Huang, Optimizing the treatment of landfill
14 leachate by conventional Fenton and photo-Fenton processes, *Sci. Total Environ.* 407
15 (2009) 3473-3481.
- 16 [34] J. Hoigne, H. Bader, Rate constants of reactions of ozone with organic and
17 inorganic-compounds in water 1: Non-dissociating organic-compounds, *Water Res.* 17
18 (1983) 173-183.
- 19 [35] M.A. Miranda, A.M. Amat, A. Arques, Abatement of the major contaminants
20 present in olive oil industry wastewaters by different oxidation methods: ozone and/or
21 UV radiation versus solar light, *Water Sci. Technol.* 44 (2001) 325-330.
- 22 [36] C.A.K. Gouvêa, F. Wypych, S.G. Moraes, N. Durán, P. Peralta-Zamora,
23 Semiconductor-assisted photodegradation of lignin, dye, and kraft effluent by Ag-doped
24 ZnO, *Chemosphere* 40 (2000) 427-432.

- 1 [37] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, Photolysis of Chloroform and
2 Other Organic Molecules in Aqueous TiO₂ Suspensions, *Environ. Sci. Technol.* 25
3 (1991) 494.
- 4 [38] M.H. Al-Malack, Determination of biokinetic coefficients of an immersed
5 membrane bioreactor, *J. Membr. Sci.* 271 (2006) 47–58.
- 6 [39] Y.F. Tsang, F.L. Hua, H. Chua, S.N. Sin, Y.J. Wang, Optimization of biological
7 treatment of paper mill effluent in a sequencing batch reactor, *Biochem. Eng. J.* 34
8 (2007) 193–199.
- 9 [40] M. Gander, B. Jefferson, S. Judd, Aerobic MBRs for domestic wastewater
10 treatment: a review with cost considerations, *Sep. Purif. Technol.* 18 (2000) 119–130.
- 11 [41] S. Judd, *The MBR book: Principles and applications of membrane bioreactors in*
12 *water and wastewater treatment*, Elsevier Ltd., Oxford, 2006.
- 13

- 1 **Table 1.** Initial characteristics of the sampled recycled paper mill effluent and the kraft
- 2 pulp mill effluent used for its experimental treatment trials.

Parameter	Recycled paper mill effluent	Kraft pulp mill effluent
tCOD (mgO ₂ ·L ⁻¹)	2319 ± 618	1749 ± 435
sCOD (mgO ₂ ·L ⁻¹)	2031 ± 459	1532 ± 328
BOD ₅ (mgO ₂ ·L ⁻¹)	959 ± 394	850 ± 370
VFA (mg·L ⁻¹)	347 ± 187	285 ± 54
Conductivity (μS·cm ⁻¹)	2322 ± 396	3553 ± 255
Alkalinity (mgCaCO ₃ ·L ⁻¹)	479 ± 184	83 ± 3
TSS (mg·L ⁻¹)	344 ± 261	314 ± 123
Total Nitrogen (mg·L ⁻¹)	11 ± 2	4 ± 1
Phosphorus-PO ₄ (mg·L ⁻¹)	1 ± 1	0.88 ± 0.5
Sulphates (mg·L ⁻¹)	496 ± 110	276 ± 38
pH	7.8 ± 0.4	5.0 ± 1.1

Figure captions

Figure 1. COD reduction obtained along the treatment of the effluent from a recycled paper mill by ozonation.

Figure 2. COD removal obtained along the treatment of the effluent sampled at a kraft pulp mill by ozonation.

Figure 3. COD reduction achieved in the UV-photocatalytic treatment of effluents from a recycled paper mill (effluent 1) and a kraft pulp mill (effluent 2).

Figure 4. COD removal results for the solar photocatalytic treatment performed at an initial pH=7 of effluents from a recycled paper mill (effluent 1) and a kraft pulp mill (effluent 2).

Figure 5. COD and BOD₅ concentration contents during the start-up piloting of the MBR.

Figure 6. Zhan Wallens biodegradability test applied to the effluent from the recycled paper mill whether having previously been oxidized by ozone (A), solar photocatalysis (B), or not.

Figure 7. Degradation efficiency results of the MBR biological treatment of the effluent from a recycled paper mill, and the oxidation post-treatment of its permeate by solar photocatalysis and ozonation.

Figure 8. Comparison of solar photocatalysis and ozonation as pre- and post-treatment alternatives of the MBR biological treatment of the effluent of a recycled paper mill.

FIGURE 1

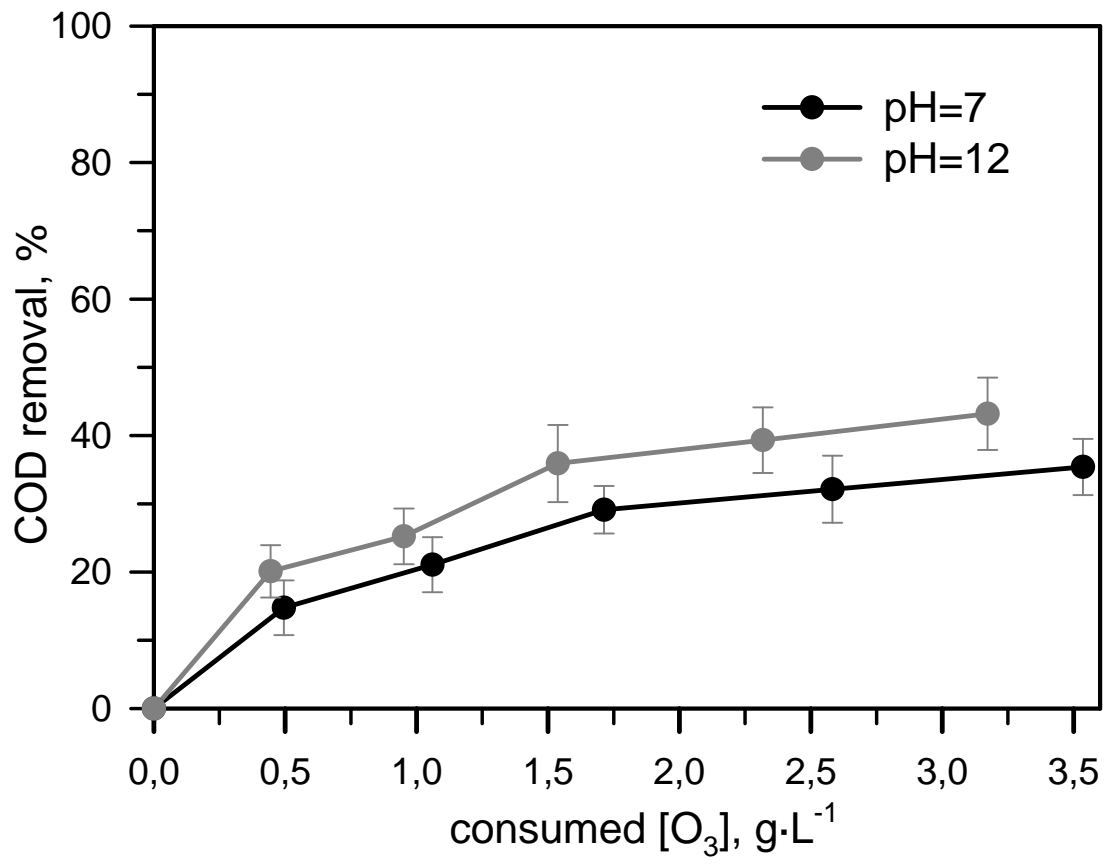


FIGURE 2

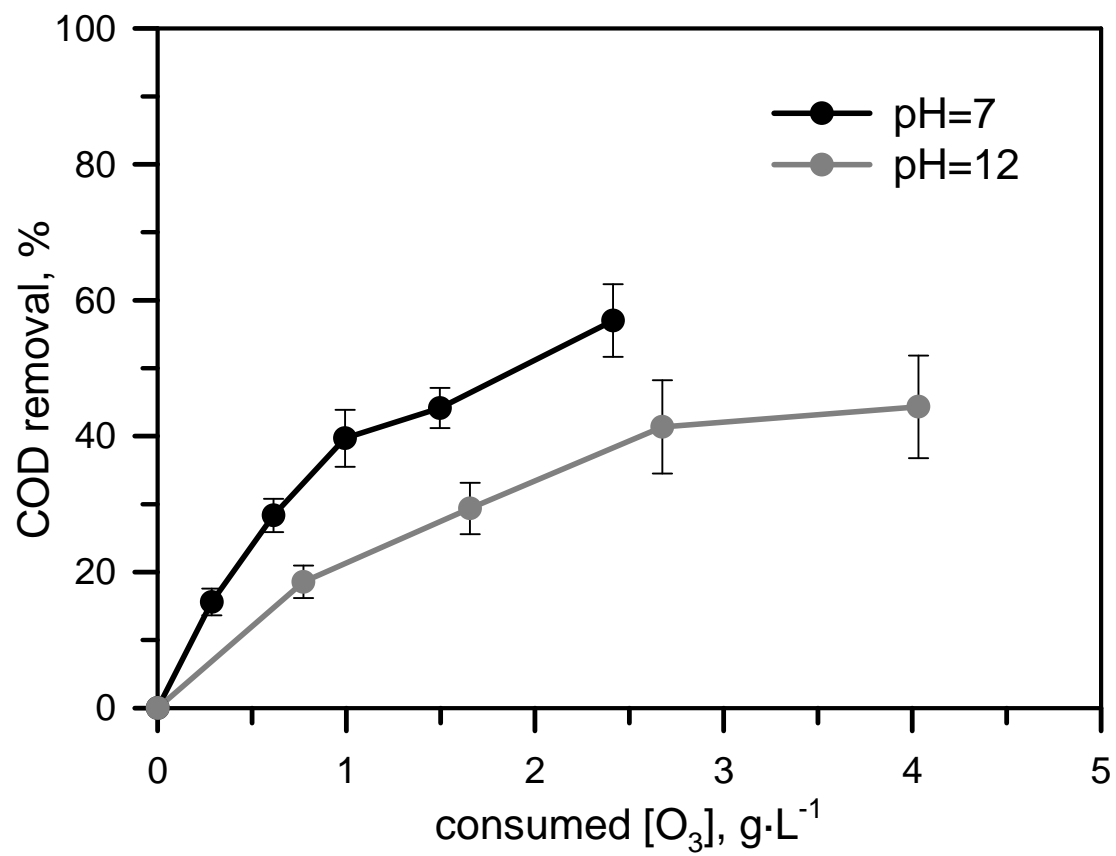


FIGURE 3

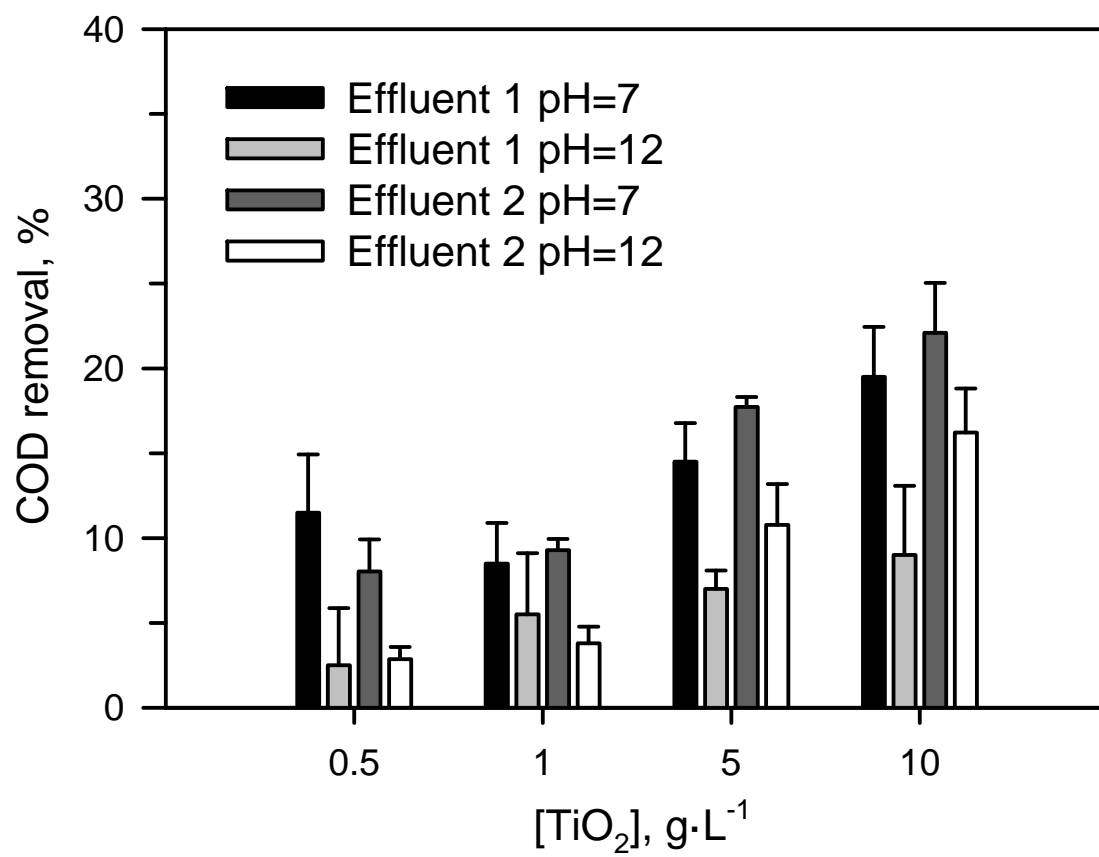


FIGURE 4

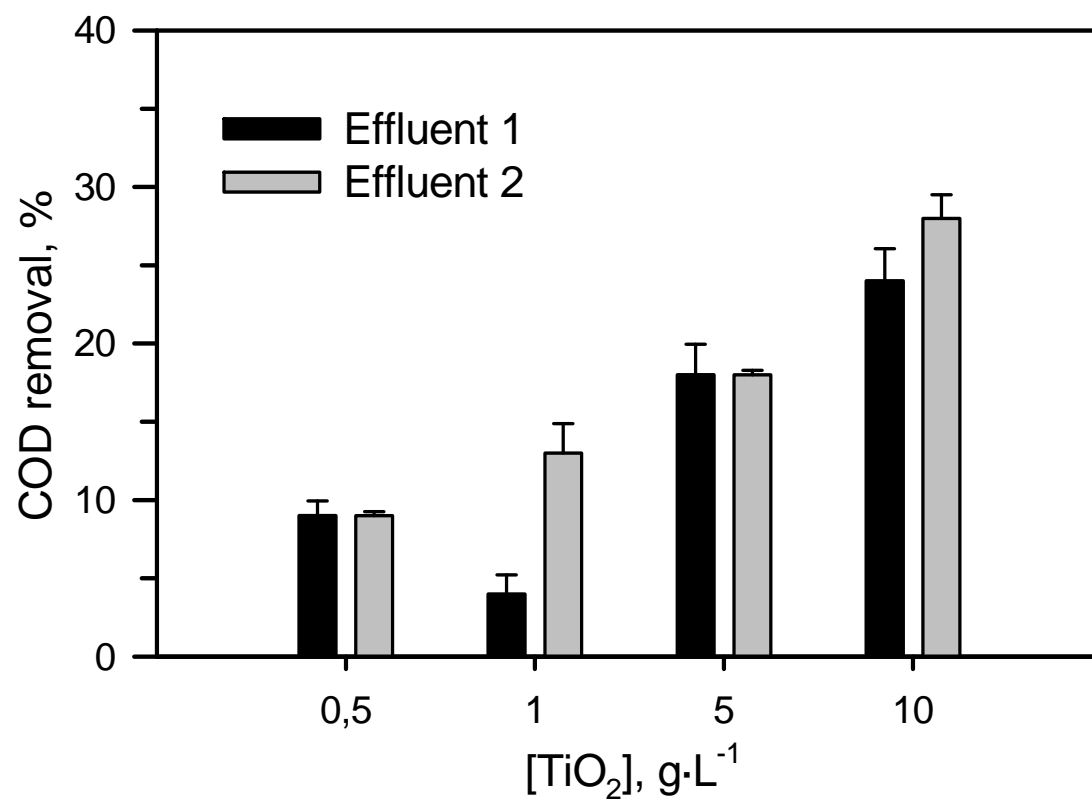


FIGURE 5

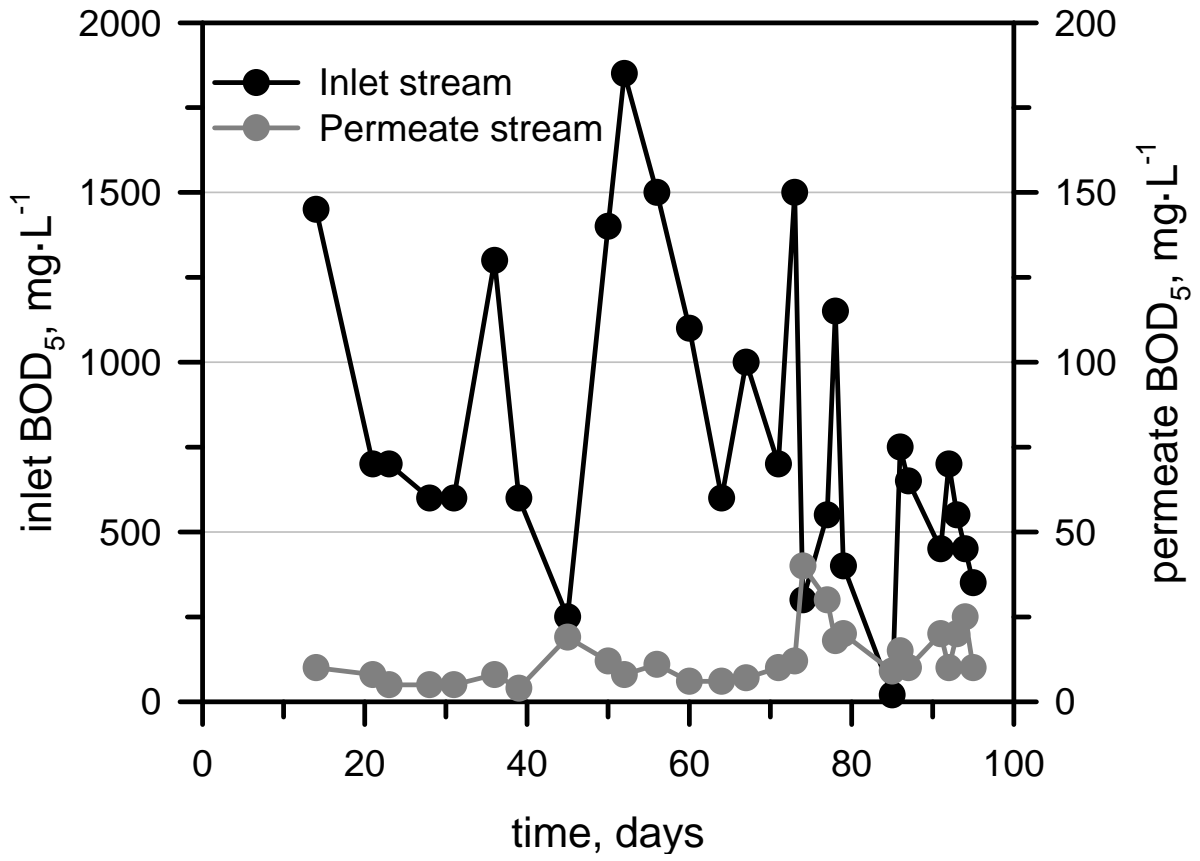


FIGURE 6

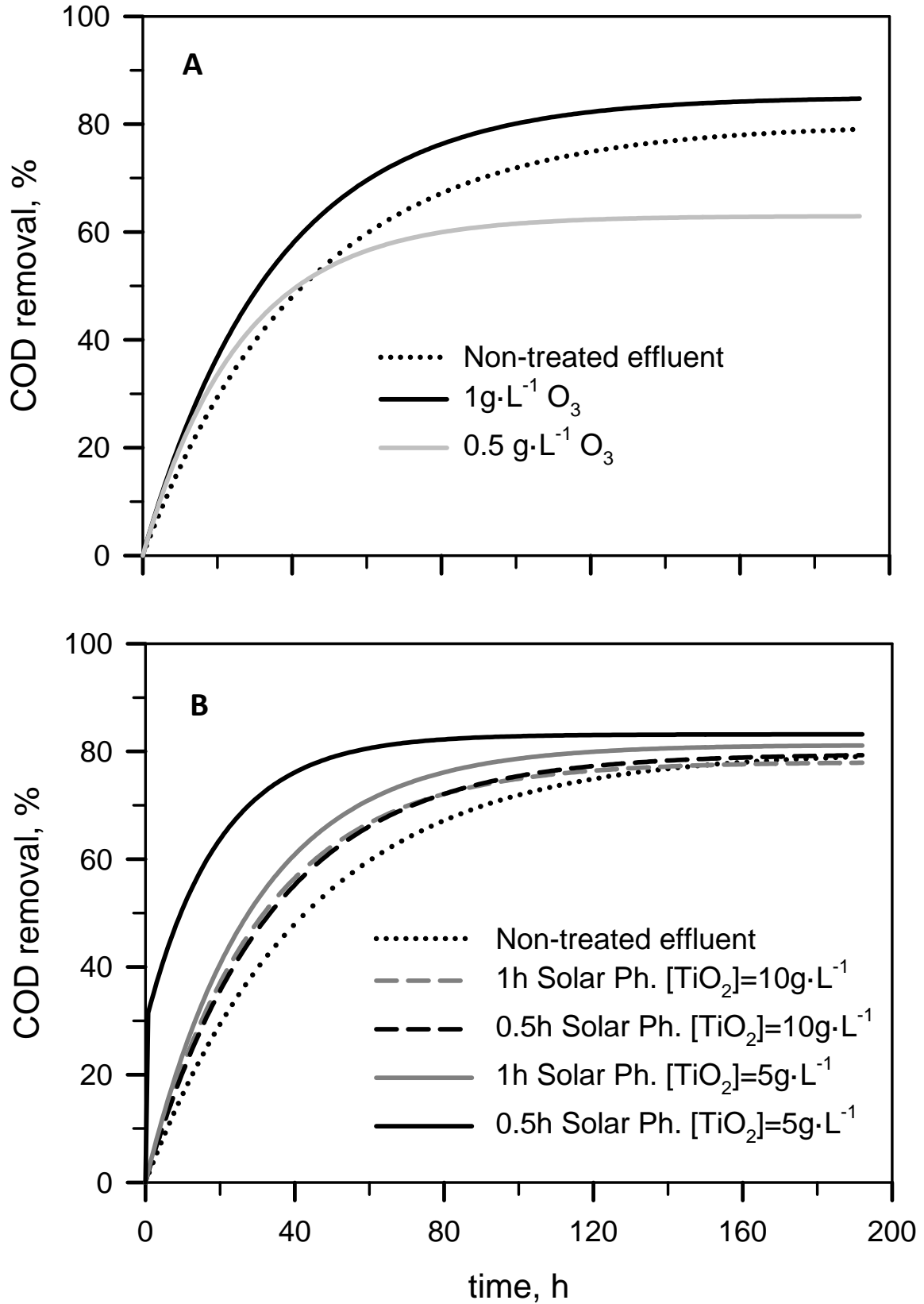


FIGURE 7

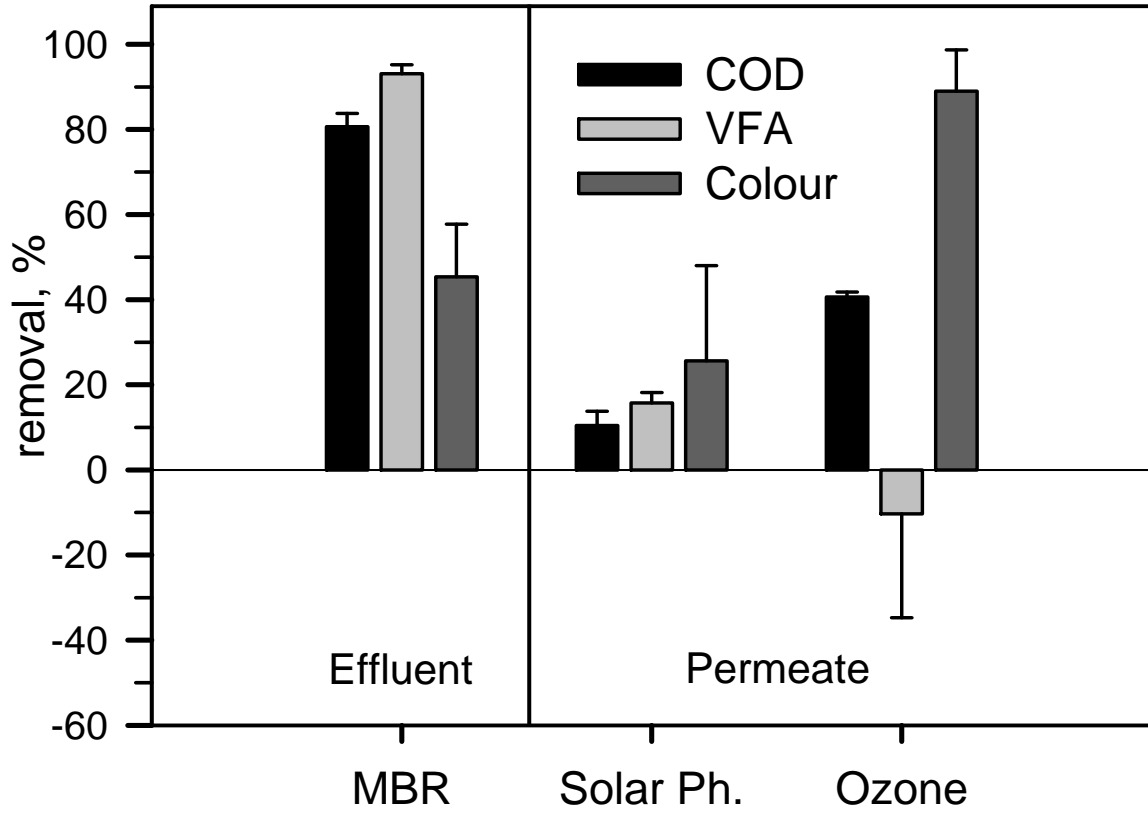


FIGURE 8

