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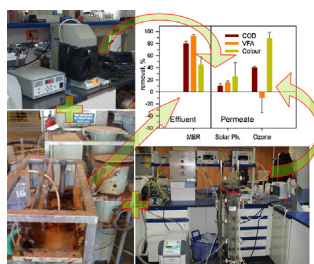
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HIGHLIGHTS

- 2.4 g O_3 L^{-1} achieved about a 60% COD removal treating a kraft pulp mill effluent.
- 10 g TiO_2 L^{-1} produced a COD removal <30% treating pulp and paper effluents.
- The composition of pulp and paper mill's effluents influenced its AOPs treatment.
- AOPs as pre-biological treatment did not result in significant better results.
- Very good COD and colour removals (>90%) were achieved combining MBR + ozonation.

GRAPHICAL ABSTRACT

ABSTRACT

The closure of water circuits within pulp and paper mills has resulted in a higher contamination load of the final mill effluent, which must consequently be further treated in many cases to meet the standards imposed by the legislation in force. Different treatment strategies based on advanced oxidation processes (ozonation and TiO_2-photocatalysis), and their combination with biological treatment (MBR), are herein assessed for effluents of a recycled paper mill and a kraft pulp mill. Ozone treatment achieved the highest efficiency of all. The consumption of 2.4 g O_3 L^{-1} resulted in about a 60% COD reduction treating the effluent from the kraft pulp mill at an initial pH = 7; although it only reached about a 35% COD removal for the effluent of the recycled paper mill. Otherwise, photocatalysis achieved about a 20–30% reduction of the COD for both type of effluents. In addition, the effluent from the recycled paper mill showed a higher biodegradability, so combinations of these AOPs with biological treatment were tested. As a result, photocatalysis did not report any significant COD reduction improvement whether being performed as pre- or post-treatment of the biological process; whereas the use of ozonation as post-biological treatment enhanced COD removal a further 10%, summing up a total 90% reduction of the COD for the combined treatment, as well as it also supposed an increase of the presence of volatile fatty acids, which might ultimately enable the resultant wastewater to be recirculated back to further biological treatment.

1. Introduction

Despite the great efforts made by the paper industry to close its water circuits, it still remains the second largest sector demanding water use [1]. Therefore, further challenges should still be

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faced up in order to keep meeting current standards related to the quantity and quality of discharged wastewater [2], and developing innovative technologies for reusing and/or recycling wastewater within the process in order to minimize the environmental impact of pulp and paper mills. Totally closing water circuits using current available technologies may lead to significant trouble in the process, as well as other problems related to water quality requirements. Therefore, new treatment strategies should aim to remove biodegradable high molecular weight (HMW) organic compounds, as well as low molecular weight (LMW) recalcitrant organic matter [3].

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

Moreover, the use of AOPs within pulp and paper mills should take into account the influence of wastewater composition on its potential treatment. Pulp industry effluents, such as those outflowing from wood chemical pulping processes, generate more than a 40% low biodegradable organics within the total organic matter content present in the final effluent [9]. On the other hand, effluents from paper mills using recovered paper as raw material are rather characterized by the presence of biodegradable starch-related products than by their content of lignin compounds [10]. In addition, it is also important to consider the efficiency of the process itself and the development of adequate protocols for using these processes in mills with a high degree of circuits closure [11]; as well as take into good account its economical assessment.

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

Complementarily, the application of TiO_2-photocatalytic treatment within the pulp and paper industry has previously been reported to show an efficient reduction of colour and dissolved organic carbon when heterogeneous TiO_2-photocatalytic processes have been applied to different types of effluents and lignin-containing solutions; as well as a rapid decrease of their toxicity and biodegradability improvement have also been addressed [14–17].

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

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

A comparative essay is herewith reported considering two very different effluents from pulp and paper industry (a kraft pulp mill,

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

Parameter	Recycled paper mill effluent	Kraft pulp mill effluent
tCOD (mg O_2 L^{-1})	2319 ± 618	1749 ± 435
sCOD (mg O_2 L^{-1})	2031 ± 459	1532 ± 328
BOD_5 (mg O_2 L^{-1})	959 ± 394	850 ± 370
VFA (mg L^{-1})	347 ± 187	285 ± 54
Conductivity (μS cm^{-1})	2322 ± 396	3553 ± 255
Alkalinity (mg $CaCO_3$ 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

and a 100% recycled paper mill effluents) in order to assess the influence of wastewater composition on AOPs efficiency. In addition, combination alternatives of AOPs and MBR technologies are also reported for the recycled paper mill effluent.

2. Materials and methods

2.1. Material and analytical methods

All used chemicals were of analytical grade and supplied by PANREAC S.A. (Barcelona, Spain). The catalyst AEROXIDE® TiO_2 P 25 was supplied by Evonik Degussa GmbH (Essen, Germany). All solutions were prepared in ultrapure water and preserved in the dark.

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

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

2.2. Experimental procedures

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

2.2.1. Ozonation

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

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

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

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

2.2.2. Photocatalysis

The photocatalytic process was performed in a reactor with a 450-W high-pressure mercury immersion lamp from ACE-glass (Vineland, USA). The total radiated power in the visible and UV regions was 159.4 W (47.5 and 52.5%, respectively). Major emission bands (>3%) were located at 578.0 nm (12.5%), 546.1 nm (15.4%), 435.8 nm (12.7%), 404.5 nm (6.9%), 366.0 nm (16.1%), 313.0 nm (8.3%), 302.5 nm (4.5%), and 253.7 nm (3.6%). A total photon flux of 1.1×10^{20} photon s^{-1} was calculated, as described in Liang et al. [25], to flow inside the photochemical reactor.

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

Aeroxide® TiO$_2$ P25 (Evonik Degussa GmbH, Essen, Germany) was used as the catalyst of the reaction. The main properties of this product are: BET surface area = 50 m^2/g, pore volume = 0.25 m^3/g, and mean particle size of ca. 30 nm. The concentration of TiO$_2$ and reaction time were optimized at the same two different initial pH values (7 and 12) justified for ozonation, and at a constant temperature of 25 °C. pH, redox potential, and dissolved oxygen were measured on-line during treatment using appropriate probes (ProODO YSI Inc., OH, USA). Each photocatalytic trial was performed for 5 h. Samples were taken every hour for COD, colour, and VFA determination.

2.2.3. Solar photocatalysis

Solar photocatalysis trials were carried out in a solar simulator equipped with a Xenon lamp (300 W) supplied by Newport (Irvine, USA). Intensity and power could be pre-selected for each experimental run, and a filter was used to correct the illuminator out to obtain a solar spectrum under ideal conditions (ASTM E490-73a). The total radiated power in the visible and UV regions was 106.5 W (51.7 and 48.3%, respectively). Major emission bands (>3%) were located at 578.0 nm (17.4%), 546.1 nm (16%), 435.8 nm (10.9%), 404.5 nm (7.5%), 366.0 nm (6.3%), 334.1 nm (4.4%), 313.0 nm (3.9%), 302.5 nm (3.7%), 296.7 nm (3.6%), 289.4 nm (3.2%), and 280.4 nm (3.0%). A total photon flux of 6.8×10^{19} photon s^{-1} was calculated,

as described in Liang et al. [25], to flow inside the photochemical reactor.

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

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

2.2.4. Biodegradability test

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

The functional power of the activated sludge was checked running a parallel test using ethylene glycol as reference substance. Its biodegradability at least reached a 70% COD reduction within the first 14 days of incubation. The ratio of removed COD to its initial value, corrected considering control results, provides the percentage of biodegradation that was achieved along the process.

2.2.5. MBR treatment

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

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

Sludge drainage was initially set at 0.4 L h^{-1} in order to regulate biomass content inside the MBR, allowing its growth until a target value of solids concentration was reached. Subsequently, values between 0.4 and 0.9 L h^{-1} were set to regulate the concentration of solids inside the tanks. The biomass inside the MBR was controlled measuring mixed liquor volatile suspended solids (MLVSS), which average value resulted 5.92 g L^{-1}. Average sludge age was 16 days at 24 h of hydraulic retention time (HRT), and 5 days at 8 h HRT. Total suspended solids (TSS), turbidity, COD, VFA, MLSS (mixed liquor suspended solids), MLVSS, total nitrogen, and phosphate contents were measured twice a week during the trials.

3. Results and discussion

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

3.1.1. Ozone treatment

The required ozone dose for an optimal treatment and the efficiency of the process therefore, were dependent on the concentration of ozone in the inlet gas, reaction time [27], and the
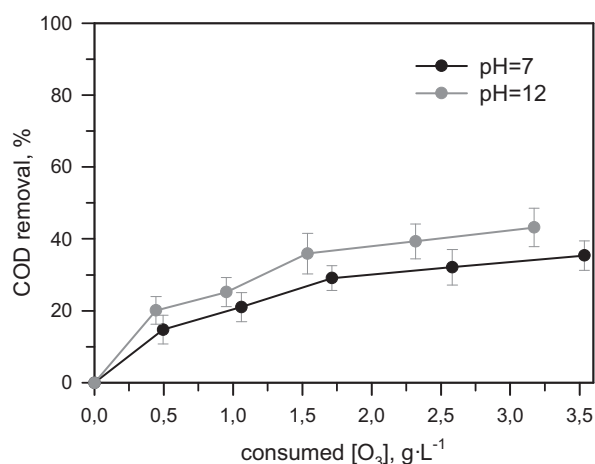
Fig. 1. COD reduction obtained along the treatment of the effluent from a recycled paper mill by ozonation.
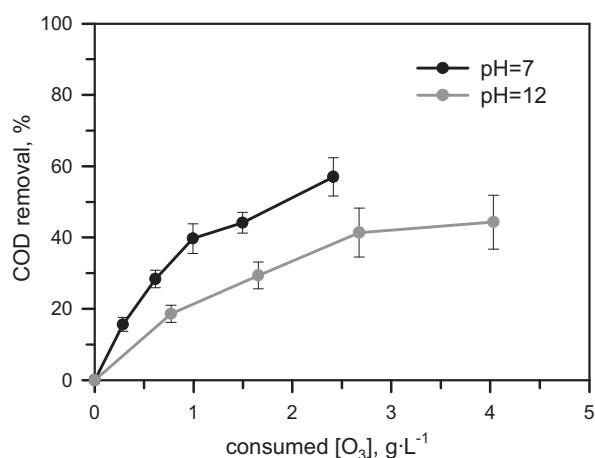

Fig. 2. COD removal obtained along the treatment of the effluent sampled at a kraft pulp mill by ozonation.

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

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

The ozone treatment of these effluents was performed through consecutive oxidation stages (Figs. 1 and 2) involving different ozone dosage consumptions depending on the organic load of the solution, and the initial pH value of the effluent. In short, two main reaction stages do really consecutively happen along the process: (1) a first one where easily oxidizable compounds were mainly degraded; and (2) a second one where oxi-recalcitrant by-products (VFA mainly [32,33]) that are formed along the process are attempted to be further oxidized [2,12]. As a result, a steepest removal of the COD was shown at the beginning of the process due to the effective degradation of oxidable products ($0.5–1.0 \, g \, L^{-1}$ O_3, depending on the type of effluent; Figs. 1 and 2); whereas reaction efficiency thereafter turned to progress smoothly as the content of oxi-recalcitrant by-products increased in the solution even though ozone dosage progressively rose as well. In fact, the limitation of TOC abatement is one of the results of this increasing accumulation of oxi-recalcitrant compounds [34]; although they are generally characterized for being highly biodegradable, which enables the possibility of adding a biological treatment stage afterwards.

3.1.2. Photocatalysis

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

Although degradation results showed the same tendency whichever light source was used, the reduction of the COD resulted slightly higher (<5%) when the solar simulator was used, particularly at the higher tested TiO_2 concentration level ($10 \, g \, TiO_2 \, L^{-1}$; Figs. 3 and 4). This particular might ultimately be explained in terms of differential characteristics of the incident light, and other properties of the used reactors that might have somehow changed the distribution and efficiency of the suspended catalyst. In this case, using the sun as light source would at least result in the reduction of the energetic cost of the treatment without meaning any efficiency loss.

In addition, similar non-significant slight COD removal differences were also found between the photocatalytic treatments of both tested effluents, resulting that higher treatment efficiency was
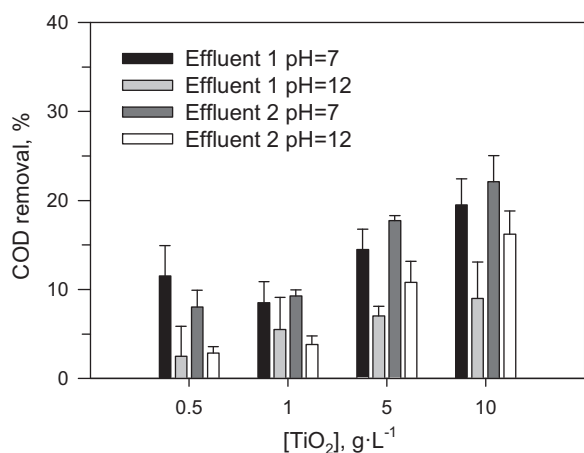
nature and concentrations of organic and inorganic compounds in the treated effluent. In short, the evolution of ozone consumption resulted different during treatment (Figs. 1 and 2) because of the continuous reaction of ozone with the changing content of organic and inorganic compounds present in the solution. As a result, the real specific ozone dose that was consumed in the reactor reached 3.6 mg O_3 per mg of removed COD for the effluent from the recycled paper mill, and 2.38 mg O_3 per mg of removed COD for the effluent from the kraft pulp mill, when $2.4 \, g \, L^{-1}$ of ozone were consumed at an initial pH = 7; as it can be calculated from Figs. 1 and 2.

In fact, the ozone treatment of the effluent from the recycled paper mill showed a lower reduction of the COD (Figs. 1 and 2), which may be attributed to its higher concentration of compounds that are difficult to oxidize (VFA, mainly); and a higher amount of bicarbonate (Table 1), which has been previously reported to produce certain scavenging effect [28]. In short, aliphatic organic compounds have previously widely been described to be difficult to oxidize by AOPs [29,30], resulting in an increase of the specific consumption of ozone, and the consequent decrease of the efficiency of the treatment. As a result, about a 60% reduction of the COD was achieved ozonating the effluent of the kraft pulp mill at an initial pH = 7 ($2.4 \, g \, L^{-1}$ of consumed ozone; Fig. 2); whereas this treatment only reached about a 35% COD removal for the effluent of the recycled paper mill (Fig. 1).

Fig. 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).
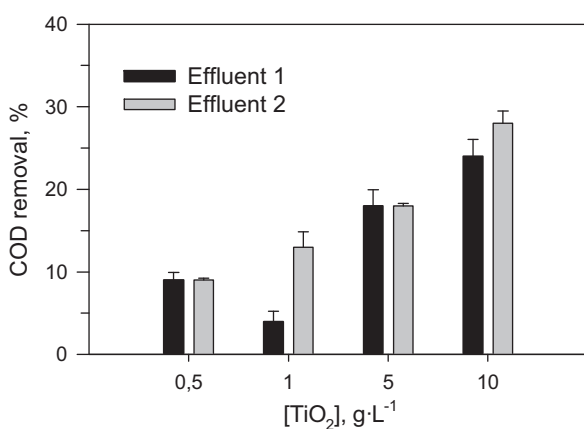

Fig. 4. COD removal results for the solar photocatalytic treatment performed at an initial pH = 7 of effluents from a recycled paper mill (effluent 1) and a kraft pulp mill (effluent 2).

achieved for the effluent from the kraft pulp mill; as it has also been reported for its ozone treatment, and may also be partially explained by the higher content of oxi-recalcitrant aliphatic organic compounds that is present in the effluent sampled at the paper mill (e.g. VFA content in Table 1).

The efficiency of these photocatalytic processes was much influenced by the dosage of TiO_2 (Figs. 3 and 4), resulting in a higher degradation of organics when the TiO_2 concentration was also higher (up to 10 g TiO_2 L^{-1}) regardless the light source (UV or solar) and initial pH value (7 or 12) that were used. These results are in accordance with those reported in Chang et al. [16] for a similar treatment of lignin powder. A concentration of TiO_2 higher than 10 g L^{-1} was not considered in the trials because it has previously been reported to cause a shadow effect interfering with the transmission of light, so the generation of electron–hole pairs cannot effectively occur under such excessive catalyst content [15,16].

Although several authors have reported good reductions of organic compounds performing photocatalytic treatment at both neutral and basic initial pH values [15,16,36], the fact is that removal of the COD resulted higher when UV-photocatalysis was performed at pH = 7 for both types of effluents (Fig. 3). This may partially have been caused by the more or less strong competition that anions, cations, and some neutral molecules exert against organic contaminants for the reactive sites on the surface of TiO_2 particles; thus decreasing the overall process efficiency whether being performed at basic or acid pH values. In short, the reaction rate
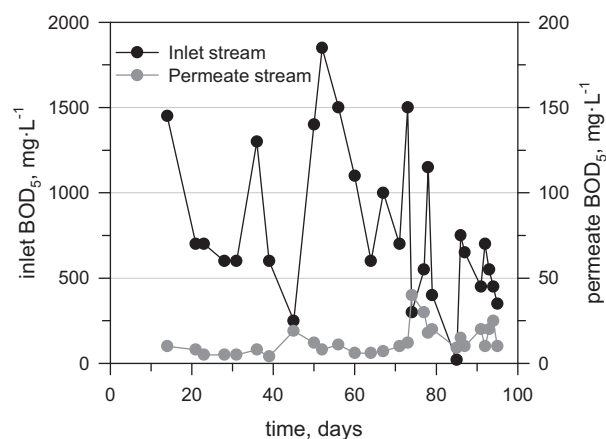

Fig. 5. COD and BOD_5 concentration contents during the start-up piloting of the MBR.

would have been slowed down by anion adsorption on the surface of the positively charged catalyst under acid conditions; whereas catalytic particles negatively charge, and the presence of cations might therefore have moderated the reaction rate, under basic pH values [37].

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

3.2.1. MBR start-up

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

The COD values measured in the permeate flowing out the MBR were very stable during all the process despite the variability of inlet wastewater quality (Fig. 5). The average sCOD value of this permeate was 250 mg O_2 L^{-1} when HRT was kept for 24 h [feed/microorganisms (F/M) ≈ 0.44 kg COD/kg MLSS day], and 500 mg O_2 L^{-1} when HRT was also evaluated at 8 h [(F/M) ≈ 1.21 kg COD/kg MLSS day], which is close to the actual value that is used in this and other similar mills.

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

BOD_5 values of permeate were often lower than 10 mg O_2 L^{-1} during the first stage of HRT = 24 h; and they resulted even slightly higher for HRT = 8 h. A total to an almost complete degradation of biodegradable organic matter was finally achieved by this treatment (Fig. 5). In addition, turbidity was in average reduced from 300 to 2 NTU; whereas suspended solids were totally removed.

The membrane always showed a good behaviour during treatment; although the optimization of this membrane treatment is
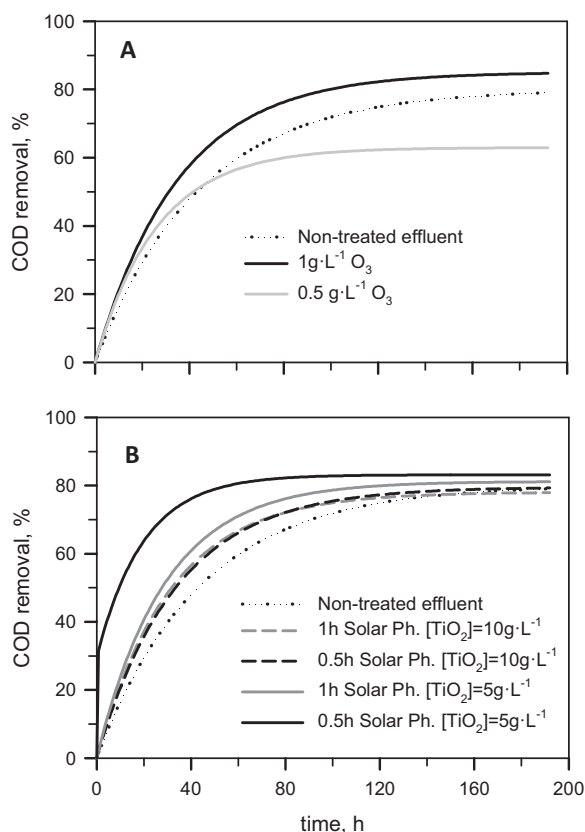
Fig. 6. Zhan Wallens biodegradability test applied to the effluent from the recycled paper mill whether having previously been oxidized by ozone (A), solar photocatalysis (B), or not.

not herewith reported because it would not result representative for industrial application. In fact, it would be necessary to perform pilot trials with membrane systems of similar characteristics than those that will be applied at industrial scale, which generally use a small number of full-scale membranes modules, in order to obtain scalable results of this type of MBR system [41].

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

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

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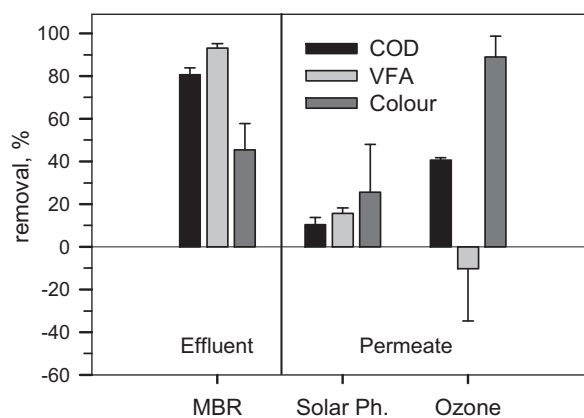

Fig. 7. Degradation efficiency results of the MBR biological treatment of the effluent from a recycled paper mill, and the oxidation post-treatment of its permeate by solar photocatalysis and ozonation.

In summary, COD reduction did not result strongly improved after any previous oxidation process; although $1\,g\,L^{-1}$ ozone treatment and $5\,g\,TiO_2\,L^{-1}$ photocatalytic process slightly enhanced biodegradability ($\approx$5%; Fig. 6). On the other hand, $10\,g\,TiO_2\,L^{-1}$ solar photocatalysis did not particularly result in higher post-biological COD reduction probably because a greater amount of biodegradable organic matter was already consumed during the oxidative process, as addressed by the better efficiency figures that were achieved when this treatment was performed standalone (Fig. 4).

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

Finally, the effluent from the recycled paper mill was firstly treated in the MBR, and the generated permeate was thereafter treated by ozonation and solar photocatalysis in order to assess the overall efficiency of this treatment strategy as well. Those reaction conditions addressing better biodegradability results (Fig. 6) were also applied in these trials, that is: (a) $1\,g\,O_3\,L^{-1}$ for ozonation, and (b) $5\,g\,TiO_2\,L^{-1}$ for a 30 min solar photocatalysis; both performed at pH = 7.

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

In summary, although all tested configurations combining biological and advanced oxidation processes resulted in the enhancement of the overall reduction of the COD, the highest COD removal was achieved treating the effluent from the recycled paper mill by a biological stage followed by the ozone treatment of the generated permeate (Fig. 8). In short, the remaining bio-recalcitrant fraction could be more efficiently ozonized when the initial biodegradable load of this effluent was previously biologically removed. Nevertheless, the biological process was able to efficiently remove most of its contaminant load; so ozone post-treatment would only be required when very stringent discharge requirements, in both quantity and/or quality terms, may be imposed.
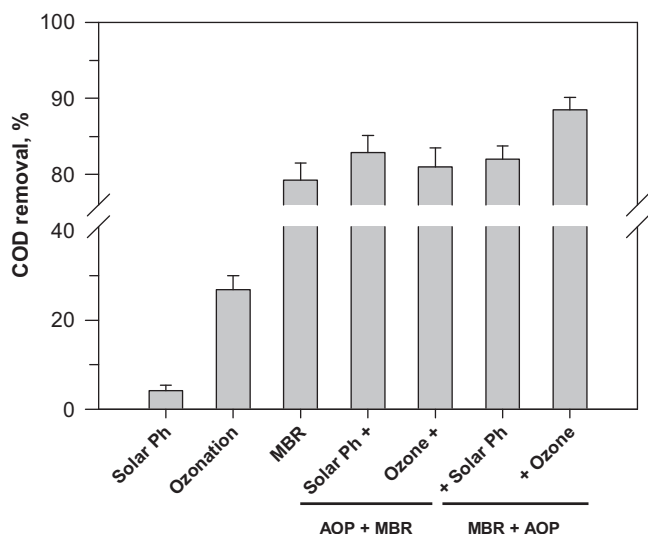
Fig. 8. Comparison of solar photocatalysis and ozonation as pre- and post-treatment alternatives of the MBR biological treatment of the effluent of a recycled paper mill.

4. Conclusions

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

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

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

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

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

In addition, the combination of an MBR biological stage with a TiO_2-photocatalysis post-treatment only reported a slight improvement of a further 10% reduction of the COD.

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

Acknowledgements

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