

**Comparison of different wastewater treatments for removal of selected endocrine disruptors from
paper mill wastewaters**

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ABSTRACT

There is increasing concern about chemical pollutants that have the ability to mimic hormones, the so-called endocrine disrupting compounds (EDCs). One of the main reasons for concern is the possible effect of EDCs on human health. EDCs may be released into the environment in different ways, and one of the most significant sources is industrial wastewater. The main objective of this research was to evaluate the treatment performance of different wastewater treatment procedures (biological treatment, filtration, advanced oxidation processes) for the reduction of chemical oxygen demand and seven selected EDCs (dimethyl phthalate, diethyl phthalate, dibutyl phthalate, benzyl butyl phthalate, bis(2-ethylhexyl) phthalate, bisphenol A and nonylphenol) from wastewaters from a mill producing 100% recycled paper. Two pilot plants were running in parallel and the following treatments were compared: (i) anaerobic biological treatment followed by aerobic biological treatment, ultrafiltration and reverse osmosis (RO), and (ii) anaerobic biological treatment followed by membrane bioreactor and RO. Moreover, at lab-scale, four different advanced oxidation processes (Fenton reaction, photo-Fenton reaction, photocatalysis with TiO₂, and ozonation) were applied. The results indicated that the concentrations of selected EDCs from paper mill wastewaters were effectively reduced (100%) by both combinations of pilot plants and photo-Fenton oxidation (98%), while Fenton process, photocatalysis with TiO₂ and ozonation were less effective (70% to 90%, respectively).

Keywords: Advanced oxidation processes, Anaerobic and aerobic biological treatment, Endocrine disruptors, Membrane filtration, Paper mill wastewaters

INTRODUCTION

In recent years, it has been reported that some chemicals may cause disruption to endocrine systems and that they may affect the hormonal control and development of aquatic organisms, wildlife and even human beings. ^[1-2] Most of the chemicals affecting endocrine activity are mutagenic and highly carcinogenic. They can cause testicular and prostate cancers, cryptorchidism, hypospadias, endometriosis, shortened menstrual cycles and female breast cancer. ^[2-3] Chemicals with endocrine activity have often been described as endocrine-disrupting compounds (EDCs), and they include different groups of compounds, such as polychlorinated bisphenyls, dioxins, polyaromatic hydrocarbons (PAHs), phthalates, bisphenol A (BPA), nonylphenol (NP), pesticides, alkylphenols, as well as arsenic and heavy metals such as cadmium, lead or mercury. ^[1-3]

EDCs may be released into the environment in different ways; one of the most significant sources is industrial wastewater, and the papermaking industry is not an exception. Some raw materials used for paper production contain phthalates, which function as softeners in additives, glues and printing inks. ^[4-5] PAHs may be also found in printing inks. Alkylphenols are constituents of widely used defoamers, cleaners and emulsifiers, ^[4-5] while pentachlorophenol is a major component of some biocides. ^[6] The pollution level of the effluents from the papermaking industry has mainly been evaluated by cumulative parameters, such as chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), total organic carbon (TOC), conductivity, total phosphorus, total nitrogen, adsorbable organically bound halogens (AOX), and toxicity. ^[7] However, very little is known about the type and concentration of individual toxic compounds in paper mill effluents. ^[8-10]

Conventional wastewater treatment processes are not specifically designed to degrade traces of dangerous organic contaminants, ^[11] so the latter are consequently consumed by aquatic organisms, and thereby represent a hazard to the whole food chain. Activated sludge systems have been successfully applied to treat a wide variety of wastewaters; more than 90% of the municipal and industrial wastewater treatment plants use this treatment type as an important part of their treatment train. ^[12-13] Activated sludge systems have been widely used for the degradation of organic compounds from paper mill wastewaters. ^[7, 10] Several microorganisms, including bacteria, fungi and yeasts, predominantly aerobic microorganisms, are known for their ability to degrade hydrocarbons to carbon dioxide, water and bacterial cells. ^[14] Biological degradation occurs aerobically by biological oxidation in activated sludge, or anaerobically in the sewage system or anaerobic sludge digester. Removal pathways for organic pollutants during aerobic treatment include adsorption onto the microbial flocks and removal in the waste sludge, biological or chemical degradation, and transformation and volatilization during aeration. ^[15] In anaerobic treatment, the organic pollutants are mixed with large quantities of microorganisms, but here, air is excluded. Under these conditions, anaerobic bacteria are capable of converting the organic waste to carbon dioxide and methane gas. Anaerobic filters, up-flow sludge blankets, fluidised beds, anaerobic lagoons, and anaerobic contact reactors are methods that use anaerobic processes that are commonly used to treat pulp and paper mill effluents. ^[7] According to Vidal and Diez ^[16] the proportion of EDC degradation by primary settling, aerating volatilization, chemical precipitation, and sludge absorption is relatively small; however the majority of EDC degradation from wastewater is regarded as biodegradation. ^[17-18] Incomplete removal of EDCs by existing biological wastewater treatment plants (BWTPs) not only results from the fluctuation of EDC levels in the influent, but also from the processes in BWTPs and from operational conditions. ^[19] The biodegradability by anaerobic treatment is strongly dependent on the characteristics of the wastewater ^[16] furthermore; this biodegradation is influenced also by numerous chemical factors, such as structural properties and environmental factors. ^[20]

Investigations of appropriate treatment methods that can be integrated into water and wastewater treatment facilities to prevent the release of EDCs into the natural waters are essential. In particular, membrane filtration technologies and advanced oxidation processes (AOPs) have recently shown promising results in the removal and/or degradation of refractory pollutants from effluents of BWTPs

and/or surface waters. [21] Membrane filtration technologies, such as reverse osmosis (RO) and ultrafiltration (UF) have also been shown as promising alternatives for removing micro-pollutants. [22] RO will provide almost complete removal, but the higher energy consumption required is an important drawback to be considered. Compared to conventional wastewater treatment, membrane bioreactors' (MBRs) remarkable advantage is the high quality of effluent, including extremely low EDC concentrations without chemical treatment. [23] AOPs are based in the generation of hydroxyl radicals in sufficient quantity to produce the chemical transformation of contaminants. [24] Hydroxyl radicals are non-selective and thus readily attack the different compounds in the solution to convert them to less complex and usually less harmful intermediate products. With proper design of operation conditions, it is possible to mineralise the target organic pollutant to CO₂. [21] AOPs as Fenton processes, photocatalysis catalysed by TiO₂ and ozonation have been used in the contaminated wastewater remediation of a broad spectrum of organic compounds and EDCs. [25-29]

Generally, the efficiency of wastewater treatments within the papermaking industry is evaluated by controlling COD, TOC and/or BOD₅. [9] Some data exists on biological degradation of EDCs within paper mill wastewaters. [10] However, no data were found on chemical degradation of EDCs within paper mill wastewaters with AOPs. Therefore, this research is the first one on the field of EDCs removal from paper mill wastewaters by AOPs. The objective of this study was to i) identifying the main EDCs in the effluent of a 100% recovered paper mill, ii) evaluate the treatment performance of two pilot wastewater treatment plants combining biological stage with membrane filtration (Fig. 2), and iii) evaluate the treatment efficiencies of four selected AOPs. The parameters studied were COD and seven potential EDCs (dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (BEHP), BPA, and NP).

MATERIALS AND METHODS

Selection Criteria of Investigated Endocrine Disrupting Compounds

Seven EDCs: DMP, DEP, DBP, BBP, BEHP, BPA and NP were chosen based on the requirements of the EU Water Framework Directive (2000/60/EC), [30] which will enter into force in 2015. NP and BEHP are on the list of priority substances according to Directive (2008/105/EC) [31] and BPA is identified as a substance subject to review for possible identification as priority substance or priority hazardous substance. However DMP, DEP, DBP and BBP were selected to be investigated, because it is well known from the literature that they occur in the effluents of paper industry. [4, 5, 9, 10, 32-34]

Chemicals and Standards

All chemicals used were of analytical grade and supplied by Panreac (Barcelona, Spain). TiO₂ was supplied by Evonik (Essen, Germany). All standards were of the highest purity commercially available and supplied by Sigma-Aldrich (Steinheim, Germany).

Sample Collection

Pilot plants A and B were installed in a paper mill, using 100% recovered paper as raw material, for the treatment of wastewater from the dissolved air flotation unit placed in the first water loop, which is the most contaminated water of the mill. This wastewater was also used for the experiments developed at laboratory scale.

Samples were collected before and after every step of Pilot plants A and B (Fig. 2). At laboratory scale, samples were collected before and after the treatment by four different AOPs (Fenton process, photo-Fenton reaction, photocatalysis catalysed by TiO₂ and ozone). Samples were collected in 2.5 L glass bottles for the analyses of COD and EDCs. Analyses were repeated three times for each pilot plant and

each AOP treatment in time intervals of every two to four days. Sample bottles were refrigerated during transportation to the laboratory in order to prevent chemical changes.

Sample Preparation

Prior extraction wastewater samples were filtered through 0.45 μm Albet nylon syringe filter. EDCs were solid phase extracted using 33 μm Strata-X cartridges (200 mg/6 mL, flow rates 3-5 mL/min) supplied by Phenomenex (Torrance, USA) and Oasis HLB cartridges (500 mg/6 mL, flow rates 3-5 mL/min) supplied by Waters (Milford, USA). Sample extracts were derivatized in a test tube with the addition of *N,O*-bis(trimethyl-silyl)trifluoroacetamide (BSTFA). After derivatization, the extract was ready for injection into the gas chromatography-mass spectrometry (GC-MS) system (Fig. 1).

Analysis of Chemical Oxygen Demand

COD was measured, according to the Standard Methods for the Examination of Water and Wastewater, [35] using the colorimetric method at 600 nm with an Aquamate-spectrophotometer (Thermo Scientific AQA 091801, Waltham, USA).

Gas Chromatography-mass Spectrometry

For determination of EDCs, an Agilent 7890 GC-MS (Santa Clara CA, USA) system with an auto sampler was used. Analytes were separated on a DB5-MS column (30 m x 0.25 mm ID x 0.25 μm) using a 1 mL/min helium flow and temperature program with an initial temperature of 50 $^{\circ}\text{C}$ (4 min), a heating rate of 8 $^{\circ}\text{C}/\text{min}$ and final temperature of 270 $^{\circ}\text{C}$ (5 min). An injection volume of 1 μL was used for all analyses. The injector was operated in splitless mode. Phthalates, BPA and NP were identified by the characteristic mass spectra while their concentrations were calculated from the calibration curves of standard acetone solutions.

Pilot Plant Treatment Process Description

Pilot plant A consisted of a biological double-step process (anaerobic + aerobic) followed by UF and RO filtration as the final step (Fig. 2). The effluent of the anaerobic reactor was discharged into an activated sludge reactor, divided in three successive cascade basins, through which the water flowed in series. An aeration system continuously supplied oxygen to the wastewater at a rate of ≥ 2 mg/L of O_2 . The concentration of solids in the mixed liquor was kept at 2–3 g/L. A secondary sedimentation served for the separation of the activated sludge from the wastewater coming out from the biological stage. The clarified water entered a 0.04 μm UF membrane system. UF membranes were made of hollow-fibres of polyethersulfone, and worked pressurised in a dead-end mode. The RO unit was formed from three membrane modules of spiral wounded polymer with a pore size of 0.1 nm operated in cross-flow conditions.

Pilot plant B consisted of an anaerobic reactor followed by a MBR and a RO filtration as final step (Fig. 2). The effluent from the anaerobic reactor was discharged into the MBR of polyethersulfone hollow-fibre membranes of 50 nm nominal pore size. The mixed liquor was kept at 8–10 g/L. The water from the MBR entered the RO section which was formed from two membrane modules of spiral wounded polymer with a pore size of 0.1 nm operated in cross-flow conditions.

Laboratory Scale Treatment Process Description

Fenton reaction

The experiments were performed in a 3 L reactor filled with 2 L of wastewater. The water was mixed

throughout the experiments with a magnetic device. The temperature was adjusted to 25 °C, avoiding an unnecessary consumption of heating energy. Several authors have studied the effect of temperature on COD removal, reporting little influence on COD removal at temperatures varying from 25 °C to 45 °C. [36-37] pH was continuously adjusted to pH 3 (± 0.1), using 1 mol/L sodium hydroxide (NaOH) or 1 mol/L sulphuric acid. pH 3 has been reported by different authors [36-39] as optimal for Fenton process. At this pH value, the stability of hydrogen peroxide (H_2O_2) and the solubility of iron are optimal. After temperature and initial pH adjustment, ferrous sulphate (FeSO_4) was added to reach the target ferrous ion (Fe^{2+}) concentration, corresponding to $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ ratios of 1.0, 1.5 and 2.0. A ratio of 1.5 was previously determined as optimal for the development of the Fenton process in different wastewaters. [36-37]. H_2O_2 was added in batch mode until the target concentration was reached, which was calculated based upon the stoichiometric ratio according to COD [40] of wastewater: $1 \text{ g COD} = 1 \text{ g O}_2 = 0.03125 \text{ mol O}_2 = 0.0625 \text{ mol H}_2\text{O}_2 = 2.125 \text{ g H}_2\text{O}_2$. Therefore $\text{COD (mg/L)} \times 2.125 = \text{mg/L of H}_2\text{O}_2$. Just before the addition of H_2O_2 , Fe^{2+} , total iron concentration, COD, and EDCs were measured. This was set as a reaction time of zero. Aliquots of the treated water were taken at pre-defined time intervals with a syringe. Each aliquot was split into two portions. The first portion was filtered through a 0.45 μm Albet nylon syringe filter to collect the filtrate for determination of the residual H_2O_2 , Fe^{2+} , and total iron content. The other non-filtered portion was adjusted to pH=8 with 10 M NaOH, stirred in a beaker for 20 min with a magnetic stirring bar, and centrifuged for 10 min at 2000 rpm for the analysis of turbidity, COD, EDCs, and H_2O_2 in the supernatant. Measured value of H_2O_2 was used to correct COD determinations according to Hermosilla et al. [37]

Photo-Fenton reaction

The experimental protocol for photo-Fenton was the same as the one described above for conventional Fenton with the additional use of a 450 W high-pressure mercury immersion UV lamp (7825-34, ACE-glass, Vineland, USA) located vertically in the centre of the reactor. The UV lamp was enclosed inside a quartz glass vessel through which the water was circulated in order to reduce the excessive heat generated during the UV irradiation. The entire assembly was in a safety cabinet (7836-20, Ace-glass, Vineland, USA). After temperature and initial pH adjustment, FeSO_4 was added to reach the target Fe^{2+} concentrations, corresponding to an $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ ratio of 32 that has been shown as optimal for the treatment of different wastewaters. [37] The irradiation of UV light allows the reduction of ferric to ferrous iron in photo-assisted Fenton processes. [38-41] Moreover, the increase of turbidity reduces the efficiency of the treatment. [40] Therefore, a lower $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ ratio is needed for the optimization of the photo-Fenton process. H_2O_2 was added in batch mode until the target concentration was reached, which was calculated according to Kim et al., [40] as described above for the conventional Fenton reaction. The influence of the double amount of H_2O_2 ($\text{COD (mg/L)} \times 4.250 = \text{mg/L of H}_2\text{O}_2$) was tested for the photo-Fenton process. The UV lamp was switched on simultaneously when the H_2O_2 was added. Just before the addition of H_2O_2 ; Fe^{2+} , total iron concentration, COD and EDCs were measured. This was set as a reaction time zero. Aliquots of the treated water were taken at pre-defined time intervals with a syringe. Each aliquot was split into two portions. The first portion was filtered through a 0.45 μm Albet nylon syringe filter to collect the filtrate for the determination of the residual H_2O_2 , Fe^{2+} , and total iron content. The other non-filtered portion was adjusted to pH = 8 with 10 M NaOH, stirred in a beaker for 20 min with a magnetic stirring bar, and centrifuged for 10 min at 2000 rpm for the analysis of turbidity, COD, EDCs, and H_2O_2 in the supernatant.

Photocatalysis with TiO_2

Samples were filtered through 1 μm glass microfiber filters (Filter-lab MFV) prior to the treatment with TiO_2 . Photocatalysis with TiO_2 is a less oxidative process than conventional Fenton and photo-Fenton processes; therefore, it is necessary to improve the efficiency of the transmission of the UV light. In a full scale treatment, suspended solids can be removed by normal filtration systems as sand filters; 5 and 10 g/L of TiO_2 were added to the samples, which were UV irradiated with a 450 W high-pressure mercury

immersion lamp (7825-34, ACE-glass, Vineland, USA) for 180 min. The entire assembly was in a safety cabinet (7836-20, Ace-glass, Vineland, USA). The efficiency of the photocatalysis process and the required reaction time for its maximization are influenced by the dosage of TiO₂.^[42] The degradation of organic compounds is improved until an excessive catalyst dosage causes a shadow effect interfering with the transmission of UV light; therefore, electron-hole pair generation cannot effectively occur. It has been reported that 10 g/L TiO₂ is the optimal level for the treatment of lignin powder.^[42] Aliquots of the treated water were filtered through 0.45 µm filters every 30 min from the beginning of the trial for measuring turbidity, COD, and EDCs.

Ozonation

Ozonation experiments were conducted in a glass jacketed cylindrical bubble reactor (height = 1 m, diameter = 5 cm) with a continuous feed of gas (4.0 L/min) with an ozone concentration in the gas of 13 g/Nm³, produced from ordinary grade air passed through polycarbonate filters, and subsequently enriched with oxygen. The system consisted of an ozone generator (Model 6020, Rilize, Gijón, Spain), a flow controller Bronkhorst® (Model F-201AV, Ruurlo, The Netherlands), and an ozone on-line analyser (Model 964C, BMT Messtechnik GMBH, Berlin, Germany). The unconsumed ozone was sent to a catalytic ozone destructor. A peristaltic pump (Masterflex® Console Drive, Cole-Parmer Instrument Company, Illinois, USA) was used to recirculate the solution under treatment (1 L) through the reactor, and probes for the measurement of pH, redox potential and dissolved oxygen (ProODO, YSI Inc., Ohio, USA). The temperature was kept at 25 °C using a thermostatic bath (Model FL300, JULABO Labortechnik GmbH, Seelbach, Germany), which was aided by the reactor glass jacket itself. Additional experiments were performed with the addition of 50 mM of H₂O₂ into the ozonation reactor.

RESULTS AND DISCUSSION

Endocrine-Disrupting Compounds

The GC-MS analysis revealed that among the seven investigated EDCs (DMP, DEP, DBP, BBP, BEHP, BPA and NP) all seven were confirmed in the investigated raw and treated paper mill effluent. The presence of the investigated EDCs in paper mill wastewaters is in agreement with other studies of paper mill wastewaters,^[8,10,43] which indicates their high usage in different paper and board production processes, and raw material contamination.

Removal of Endocrine-Disrupting Compounds by Biological and Membrane Treatments

COD is a common parameter used for the characterization of organic matter present in paper mill effluents.^[8-10] COD in paper mill effluents depends on the raw material used, the type of paper produced and the type of paper machine.^[9] For the removal of organic load from paper mill wastewaters, an activated sludge process has been widely used.^[7, 10] Although conventional BWTPs are not designed to remove traces of dangerous organic contaminants as EDCs from wastewater, studies indicate removal efficiencies from 69% to 92% of aerobic, anaerobic or combined aerobic-anaerobic BWTPs for removal of EDCs from wastewaters.^[10, 44-45] In the case of Pilot plant A, removal efficiencies after first (anaerobic) treatment step were 63% for COD, 64% to 69% for phthalates, 68% for BPA and 64% for NP; and after second (aerobic) treatment step 75% to 80% for phthalates, 72% for BPA and 71% for NP (Fig. 3A). In the case of Pilot plant B, removal efficiencies after first (anaerobic) treatment step were 64% for COD, 65-71% for phthalates, 69% for BPA and 66% for NP (Fig. 3B). According to Soares et al.^[17] and Zhao et al.,^[18] biodegradation is the dominant mechanism of phthalates, BPA, and alkylphenols degradation in water. Vidal and Diez^[16] stated that the majority of EDC removal from wastewater is by biodegradation, and that primary settling, aerating volatilisation, chemical precipitation, and sludge absorption are in the minority. Obtained results of EDC degradation regarding activated sludge treatment steps in both pilot

plants are in agreement with Balabanič and Krivograd Klemenčič. [10]

Removal efficiencies after UF (third treatment step in Pilot plant A) were 77% for COD, 93% to 97% for phthalates, 93% for BPA and 93% for NP (Fig. 3A). High removal efficiencies of EDCs by UF are reported also by Bodzek et al. [46] and Snyder et al. [47] Removal efficiencies of EDCs from paper mill wastewaters can be compared with that of EDCs from the synthetic aqueous solution. Membrane filtration technologies, such as UF has been shown as a promising alternative for removing of different micro-pollutants. [22] Compared to conventional processes, UF's remarkable advantage is the high quality of effluent, including extremely low organic concentration, and the removal of microbes and viruses without chemical disinfection. Physical means may be advantageous for their simple operation and high removal efficiency. [22]

Removal efficiencies after MBR (second treatment step in Pilot plant B) were 90% for COD, 95% to 97% for phthalates, 90% for BPA, and 94% for NP; these values are close to the data obtained with the activated sludge combined with UF. The significant reduction in COD could be attributed to the oxidation reactions due to aeration in combination with activated sludge and the posterior treatment by UF. Obtained results also agree with those of Lew et al., [48] who observed an 88% for COD removal from wastewaters treated by MBR. According to Wintgens et al. [23] and Clara et al. [49] MBR could remove more than 80% of potential EDCs from wastewaters, which is also in agreement with obtained results. Compared to conventional wastewater treatment, the advantage of MBR is the high quality of effluent, including extremely low EDCs concentrations without chemical treatment, better control of biological activity, effluent that is free of bacteria and pathogens, smaller plant size, and higher organic loading rates; [23] however, one of the main disadvantages is its energy consumption. Conversely, removal efficiency after MBR was the same as after an aerobic treatment followed by UF, which may be a less energy-consuming process. Therefore the final definition of the treatment train at the industrial scale must be assessed in economic, environmental and viability terms.

However, for dangerous organic contaminants such as EDCs, the removal rates achieved with UF and MBR are not sufficient, and in the case when the non-removed contaminants are released to the receiving natural waters, they will be consequently consumed by aquatic organisms and through them may also enter human food chain. RO was introduced in both pilot plants as a final treatment stage and in both cases the removal of COD and EDCs was 100%. The significant drawback to be considered with RO is the high energy consumption and the formation of wastewater rejected as insufficiently sanitary, which must be further retreated. It is true that during RO treatment the concentration of EDCs will be increased in the concentrate effluent. Moreover these concentrates will produce serious problems of contamination if they are not properly managed. According with investigations presented the most suitable treatments for avoiding a posterior contamination due to these concentrates may be AOPs or advance flocculation. Almost complete removal of EDCs by RO is also reported by Comerton et al., [50] and Bolong et al.. [51] Removal of contaminants by membrane filtration technologies is not like biodegradation or chemical oxidation, as no by-products or metabolites are newly produced. According to Liu et al., [19] the rejection efficiency of EDCs by membranes strongly depends on the physico-chemical properties of EDCs, such as molecule weight, octanol/water partition coefficient (K_{ow}), water solubility, and electrostatic properties. EDC removal by the membrane filtration technologies is mainly due to size exclusion, charge repulsion, and adsorption. [19]

Laboratory Scale Advanced Oxidation Processes

According to IPPC, [52] the general Best Available Technology for pulp and paper industry wastewater treatment are considered: (a) an activated sludge system under the prerequisite that concentrated streams containing non-biodegradable compounds are pre-treated separately; (b) pre-treatment of highly-loaded, selected and segregated single wastewater streams containing non-biodegradable compounds with chemical oxidative treatments and AOPs. AOPs are well known for their capacity for oxidising and

mineralising bio-recalcitrant organic compounds. [21, 25-26, 53] In the frame of research presented in this study, four different AOPs were assessed with the intention of discovering which type of AOP treatment is the most effective for the removal of EDCs from raw paper mill wastewater. However, in the treatment of large volumes of wastewater, cost is the most important factor to be considered.

Fenton reaction

In the treatment of a large amount of wastewater ($>10 \text{ m}^3/\text{t}$), the most important factor concerned for industry is the cost. The major cost in the Fenton treatment is the chemical cost, especially the cost for H_2O_2 (Table 1). Based on such concerns, the H_2O_2 dose should be determined properly. In this study, the initial concentration of H_2O_2 was determined by optimising its molar ratio to COD ($\text{COD (mg/L)} \times 2.125 = \text{mg/L of H}_2\text{O}_2$). Previous experiments (data not shown) indicated that COD removal is not significantly increased with H_2O_2 concentrations up to $2.125 \times \text{COD (mg/L)}$, and that the COD removal increase (less than 8% for double H_2O_2 concentration) is not compensated for the increment of cost associated. The maximum duration of the wastewater treatment with the Fenton reaction in research presented in this study was 30 min, since we discovered that a 30 min treatment was enough to consume all the H_2O_2 and reach the maximum degradation of COD and EDCs. The main process variables affecting the rate of Fenton reaction are the reagents H_2O_2 , Fe^{2+} concentrations and the ratios between them. [38, 40] Increasing the concentration of H_2O_2 is important to obtain high oxidation efficiencies. If the concentration of one reactant is increased to observe its positive effect, thereby keeping the other one constant, the $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ molar ratio and hence the oxidation conditions will change significantly. [38] As seen in Figure 4A, the degradation rate increased with increasing initial H_2O_2 concentration. This is due to more hydroxyl radicals and other oxidant species being produced. According to Kim et al. [40] and Hermosilla et al. [38] $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ ratio of 1.5 is optimal for COD treatment of landfill leachate, which was confirmed also with this study for paper mill wastewater of a mill for 100% recovered paper. Treatment of wastewater with Fenton reaction at $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ ratio 1.5 and treatment time of 30 min reached the highest degradation of COD, and EDCs (75% for COD, 90% to 91% for phthalates, 91% for BPA and 90% for NP, respectively), followed by $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ ratio 1.0 (69% for COD, 81% to 84% for phthalates, 82% for BPA and 80% for NP, respectively) and $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ ratio 2.0 (63% for COD, 68% to 75% for phthalates, 71% for BPA and 67% for NP, respectively) (Fig. 4A). Sevimli [54] found 83% COD degradation in the optimal Fenton operation conditions ($\text{pH} = 4$, $[\text{H}_2\text{O}_2] = 200 \text{ mg/L}$, $[\text{Fe}^{2+}] = 100 \text{ mg/L}$, $t = 45 \text{ min}$), although this effect was observed in this study for biological treated paper mill wastewater. Wongniramaikul et al. [55] found an 87% degradation of diisobutyl phthalate (DIBP) from synthetic aqueous solution (14 mg/L) in the optimal Fenton operation conditions ($\text{pH} = 3$, $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]:[\text{DIBP}]$ molar ratio = 5:5:1, $t = 30 \text{ min}$). From Figure 4B, it is evident that removal of COD and EDCs started right after initiation of the reaction and was increasing slowly with time because at the beginning of the Fenton process, all ferrous iron reacts quickly with hydrogen peroxide producing a rapid generation of hydroxyl radicals, and therefore, a quick and extensive oxidation of organic compounds, and a fast depletion of ferrous ions as well. Consequently, the availability of ferrous iron becomes the main rate-limiting step during the process as the reduction of ferric iron is slower than the consumption of ferrous iron. [37]

Photo-Fenton reaction

The Fenton reaction generates sludge, which can be separated from the wastewater, but needs the application of a thickening process with additional operating costs, and it must be properly discarded. The use of UV light in combination with the Fenton reagent (photo-Fenton method) re-generates the ferrous iron with a reduction of the ferric form. According to Hermosilla et al., [37] the photo-regeneration of Fe^{2+} from Fe^{3+} allows reducing up to 32 times the quantity of FeSO_4 added to run an optimal Fenton treatment, thus reducing the production of iron sludge. Furthermore, the addition of UV-light to Fenton process produces additional hydroxyl radicals via photolysis. [41] Experiments were performed with two different concentrations of H_2O_2 (Fig. 5B) in order to attempt to reach a 100% COD reduction. All H_2O_2

was consumed within 60 min in the first trials ($\text{COD (mg/L)} \times 2.125 = \text{mg/L of H}_2\text{O}_2$); degradation efficiency was app. 96% (Fig. 5B). Double amounts of H_2O_2 were added in the second trials ($\text{COD (mg/L)} \times 4.250 = \text{mg/L of H}_2\text{O}_2$). All H_2O_2 was consumed within 120 min; degradation efficiency was approximately 98% (Fig. 5B). The maximum duration of the wastewater treatment with the photo-Fenton reaction was 120 min, since we found that a 120 min treatment was enough to consume all the H_2O_2 and reach the maximum degradation of COD and EDCs. According to Hermosilla et al. [38] and Ioan et al. [56], the Fenton reaction is more efficient in the presence of UV light, as UV light may promote photo-decarboxylation of ferric carboxylates and reduce ferric iron, yielding additional hydroxyl radicals by photolysis. Also in the case of study presented in this paper, the photo-Fenton reaction was more efficient in COD and EDCs degradation than the conventional Fenton reaction. This study showed that the treatment of wastewater by adding a double amount of H_2O_2 reached the highest COD and EDCs reduction efficiencies (98% for COD, 98% to 99% for phthalates, 99% for BPA and 98% for NP, respectively).

According to Hermosilla et al., [37-38] an increase of COD removal in photo-Fenton treatment is possible by adding extra quantities of H_2O_2 , although the cost of the treatment is significantly higher and an extra removal of COD may not be significant. Figure 5A shows the evolution of EDC and COD removal when the H_2O_2 dosages were tested. Ferrous iron regeneration during the photo-Fenton process produces the evolution of the Fenton reaction, and the addition of an extra amount of H_2O_2 allows continuing the reaction and to achieving a total COD and EDC reduction. After 20 min of treatment, efficiencies reached 39% for COD and 42% to 50% for EDCs. A further 20 min of treatment contributed an additional 32% for COD and 20% to 26% for EDCs; the following 20 min contributed additional 19% for COD and 16% to 20% for EDCs, while every further 20 min of treatment contributed less to the COD and EDC removal. The last 20 min of treatment contributes only an additional 0.5% for COD and 1% to 2% for EDC (Fig. 5C). Hermosilla et al. [38] found the same results, >96% COD removal treating phenol, nitrophenol and oxalic acid by optimal photo-Fenton conditions ($\text{COD} = 475 \text{ mg/L of O}_2$, $\text{pH} = 3$, $[\text{H}_2\text{O}_2] = 30 \text{ mM}$, $[\text{Fe}^{2+}] = 0.8 \text{ mM}$, $t = 60 \text{ min}$). Yang et al. [28] observed 75.8% degradation of DEP from synthetic aqueous solution (10 mg/L) in the optimal photo-Fenton conditions ($\text{pH} = 3$, $[\text{H}_2\text{O}_2] = 47.4 \text{ }\mu\text{M/min}$, $[\text{Fe}^{2+}] = 0.167 \text{ mM}$, $t = 120 \text{ min}$); the reason for which could be higher initial concentrations of DEP (10 mg/L). Chiou et al. [29] found a 92% degradation of DBP from a synthetic aqueous solution (5 mg/L) in the optimal photo-Fenton conditions ($\text{pH} = 3$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mM}$, $[\text{Fe}^{2+}] = 0.45 \text{ mM}$, $t = 90 \text{ min}$). Gkorgkolia et al. [57] found a 90% degradation of DBP from synthetic aqueous solution (2000 ppm) in the optimal photo-Fenton conditions ($[\text{H}_2\text{O}_2] = 20 \text{ mg/L}$, $[\text{Fe}^{2+}] = 1 \text{ mg/L}$, $t = 60 \text{ min}$). Katsumata et al. [26] found >90% degradation of BPA from synthetic aqueous solution (10 mg/L) in the optimal photo-Fenton operation conditions ($\text{pH} = 4$, $[\text{H}_2\text{O}_2] = 4 \text{ mM}$, $[\text{Fe}^{2+}] = 0.4 \text{ mM}$, $t = 36 \text{ h}$).

Photocatalysis with TiO_2 reagent

Treatment of wastewater with photocatalysis with a TiO_2 reagent was performed with an addition of 5 g and 10 g of powdered TiO_2 (Fig. 6A) with the intention of discovering at which amount of added TiO_2 powder COD and EDC degradation efficiencies were the highest. The measurements of COD and EDCs were performed at four different time intervals (Fig. 6B) Treatment of wastewater with an added 10g/L TiO_2 reagent and treatment time of 180 min reached the highest degradation of COD and EDCs (48%, 73% to 86%, 80% and 76%, respectively), followed by treatment with added 10 g/L TiO_2 reagent and treatment time 120 min (39%, 69% to 77%, 70% and 70%, respectively) and treatment with an added 5 g/L TiO_2 and treatment time 180 min (38%, 62% to 81%, 71% and 66%, respectively). The results showed that the removal of COD by photocatalysis with TiO_2 reagent was poor, while removal of EDCs was higher. As previously reported by different authors, [58] photocatalysis treatment may remove toxic and non-biodegradable substances to a great extent, it is also an alternative for pre- or post-biological treatment. Perez et al. [59] and Rodrigues et al. [60] applied photocatalysis by TiO_2 reagent to paper mill effluents and have obtained reductions of COD between 16% and 40%, which is in accordance with results of this study. Xu et al. [53] observed an 80% degradation of BBP from synthetic aqueous solution (1

mg/L) in the optimal photocatalysis conditions (pH = 7, [TiO₂] = 2 g/L, t = 120 min) and Lau et al. [61] observed a 100% degradation of DBP from synthetic aqueous solution in 90 min, while Chung and Chen [62] observed a 40% to 100% degradation of BEHP from synthetic aqueous solution (25–300 µg/L) in the optimal photocatalysis conditions (pH = 4, [TiO₂] = 100 µg/L, t = 150 min).

Ozonation

The paper mill effluent was exposed to ozone and ozone + H₂O₂ oxidation to determine their effectiveness for COD and EDC degradation. The measurements of COD and EDCs were performed at four different time intervals (Fig. 7B). As can be seen in Fig. 7A, limited COD and EDC degradation rates were obtained. COD and EDC degradation within first 60 min were significant, but the oxidation rate decreased as the reaction proceeded. Treatment of wastewater with added ozone with 50 mM H₂O₂ and an added treatment time of 180 min achieved the highest degradation of COD, phthalates, BPA and NP (59%, 90% to 92%, 91% and 92%, respectively), followed by treatment with ozone only and a treatment time of 180 min (38%, 74% to 79%, 78% and 76%, respectively), and treatment with added ozone with 50 mM H₂O₂ and a treatment time of 120 min (45%, 74% to 75%, 75% and 75%, respectively). The results showed that the removal of COD by ozone only and ozone with an added 50 mM H₂O₂ was not very high, while removal of EDCs was higher. As with photocatalysis, ozone may remove toxic compounds, and it may be used as pre and post- biological treatment step. Sevimli et al. [54] applied ozonation to paper mill effluents and obtained COD removal of 61% to 64%, which is more or less in agreement with results of this study. The influence of the addition of H₂O₂ to the wastewater sample for the COD and EDC degradation was low. A major disadvantage of ozonation is the relatively high cost of energy required for ozone generation (Table 1) coupled with the short half-life ozone period. Thus, ozone always needs to be generated on site.

CONCLUSIONS

Among the selected wastewater treatment methods, reverse osmosis (RO), the photo-Fenton reaction, and membrane bioreactor were the most efficient for COD and selected EDC removal, while the Fenton process, photocatalysis with TiO₂ and ozonation were less effective. The EDC removal from paper mill effluents is a process with high energy consumption, in which cost and efficiency are the key considerations for their application. RO as a final step in both pilot plants provided 100% removal for COD and selected EDCs, but the higher implied energy consumption is an important disadvantage to be considered. The process costs may be also considered the main reason that serious doubts hinder the commercial application of the photo-Fenton process. Biological treatment has proven to be the most cost effective processes. However, its removal efficiency for dangerous substances such as EDCs is not high enough. Human health and environmental quality risks associated with the presence of EDCs in industrial effluents necessitate the utilisation of new methods for their efficient reduction. As EDCs are detrimental even if present in low concentration levels, they should be seriously considered and their impact further studied.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Figure 1. Scheme of solid phase extraction and derivatization. BSTFA – *N,O*-bis(trimethylsilyl)trifluoroacetamide; GC-MS – gas chromatography-mass spectrometry

Figure 2. Scheme of Pilot plant A and Pilot plant B. DAFs: dissolved air flotation units, UF: ultrafiltration, RO: reverse osmosis, MBR: membrane bioreactor.

Figure 3. Mass removal of single treatment steps in Pilot plant A, and in Pilot plant B for chemical oxygen demand and investigated endocrine-disrupting compounds. An: anaerobic, Aer: aerobic, UF: ultrafiltration, RO: reverse osmosis, MBR: membrane bioreactor.

Figure 4. Mass removal for chemical oxygen demand and investigated endocrine-disrupting compounds used Fenton reaction. A: different $[\text{H}_2\text{O}_2:\text{Fe}^{2+}]$ ratios applied, B: time intervals applied in $[\text{H}_2\text{O}_2:\text{Fe}^{2+}]$ ratio 1.5.

Figure 5. A: Mass removal for chemical oxygen demand and investigated endocrine-disrupting compounds used photo-Fenton reaction. B: mass removal of COD at different time intervals applied, C: mass removal for chemical oxygen demand and investigated endocrine-disrupting compounds used photo-Fenton reaction in $[\text{H}_2\text{O}_2:\text{COD}]$ ratio 4.25.

Figure 6. Mass removal for chemical oxygen demand and investigated endocrine-disrupting compounds used photocatalysis with TiO_2 reagent. A: different TiO_2 concentrations applied, B: time intervals applied in concentration 10 g TiO_2 reagent/L.

Figure 7. Mass removal for chemical oxygen demand and investigated endocrine-disrupting compounds used ozonation. A: different ozone treatments applied, B: time intervals applied in ozone treatment O_3+50 mM H_2O_2 .

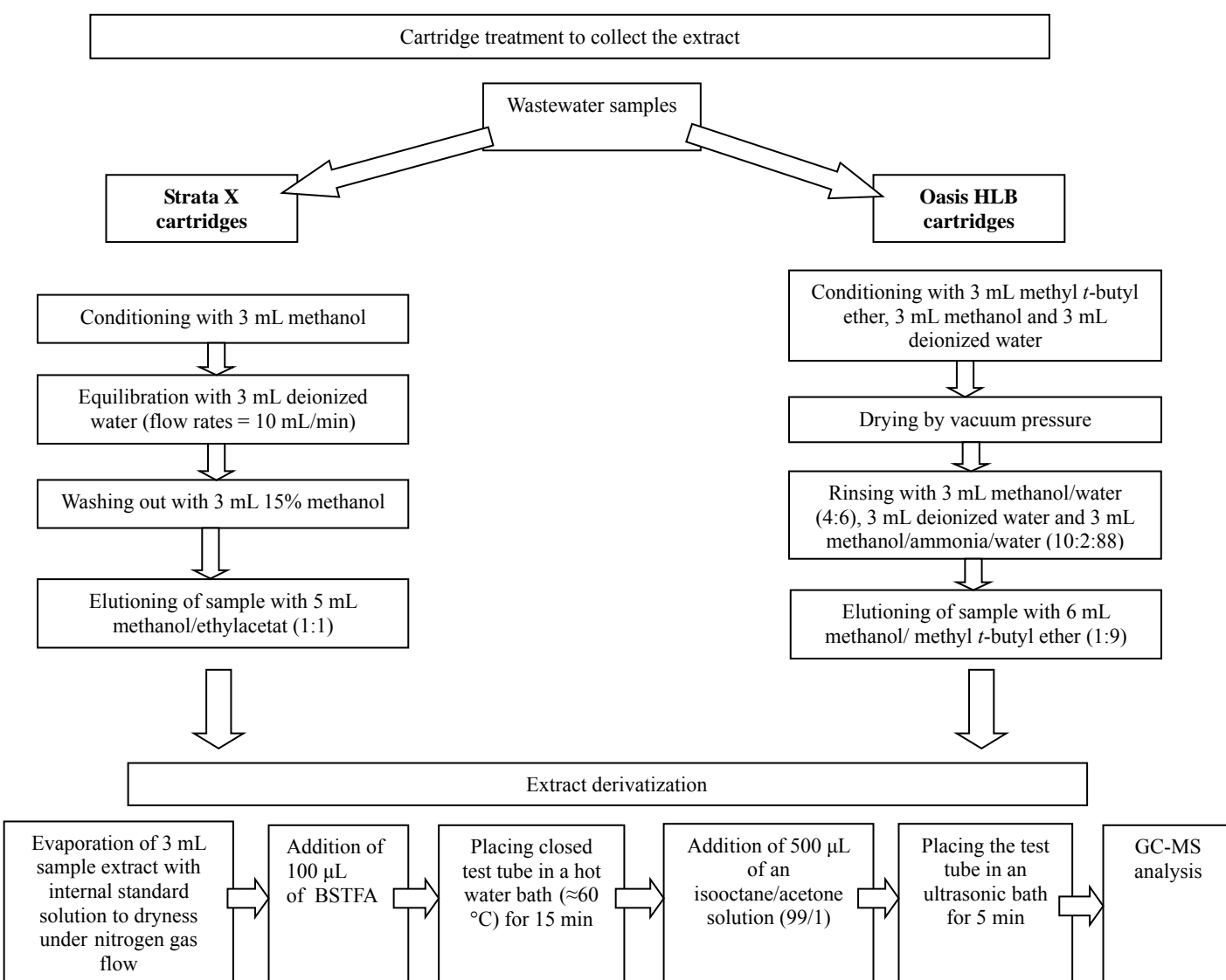


Fig. 1

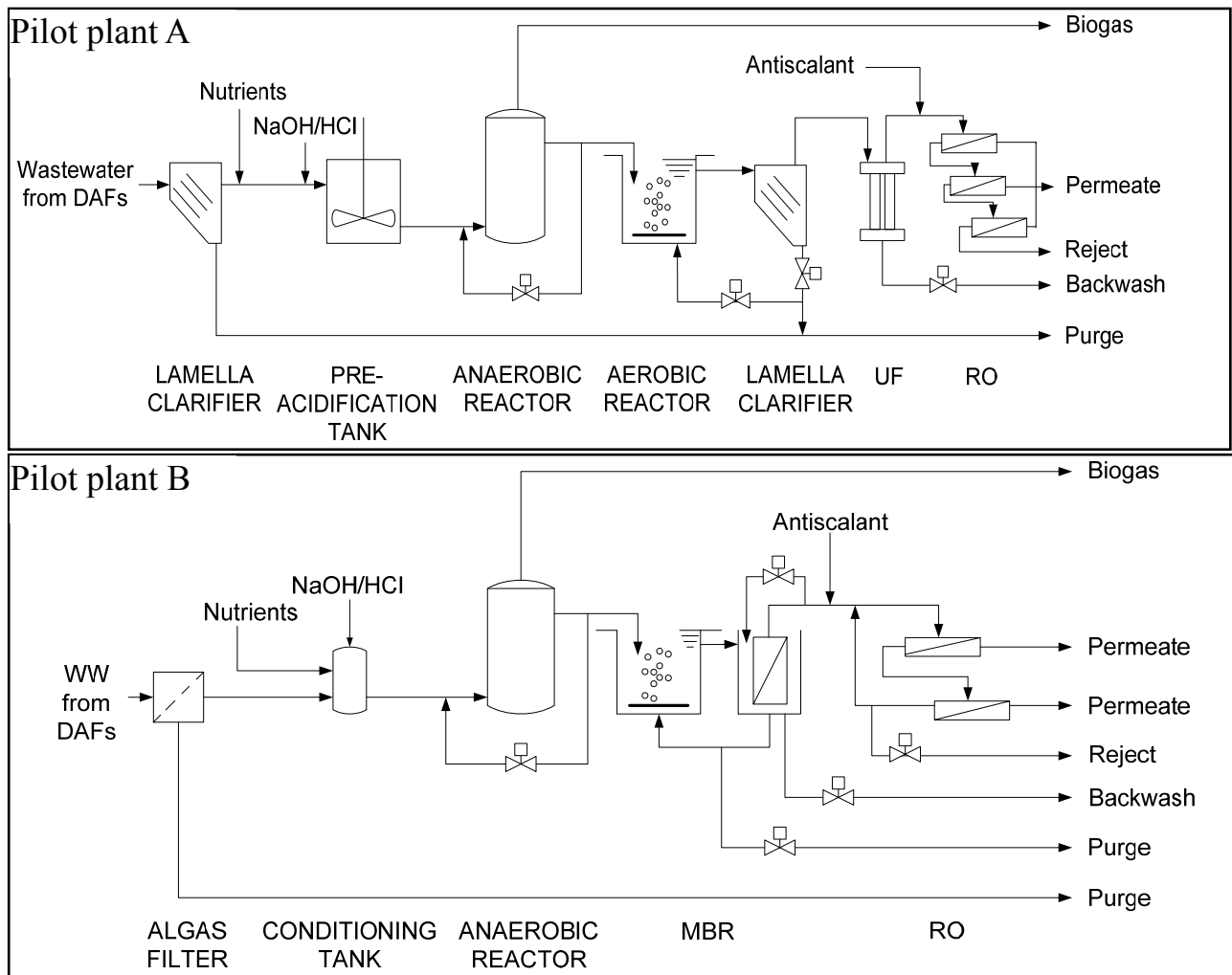


Fig. 2

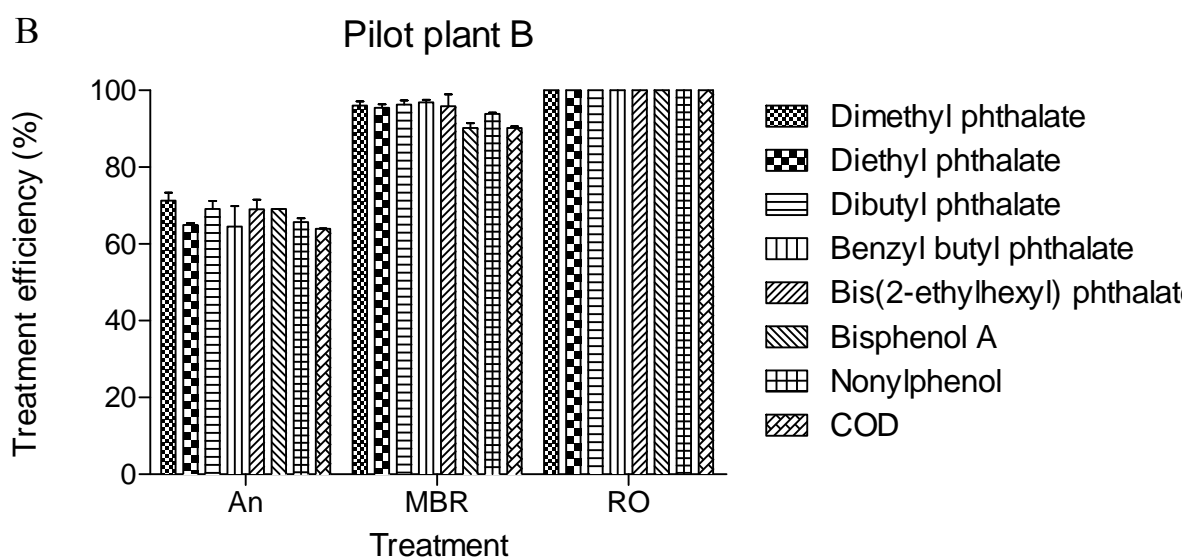
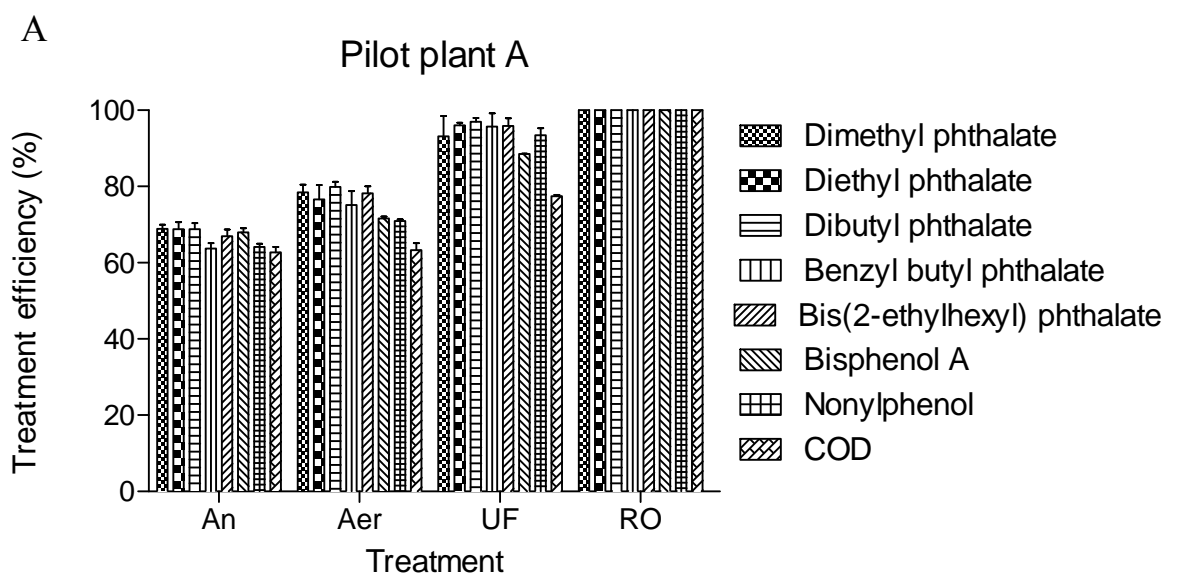


Fig. 3

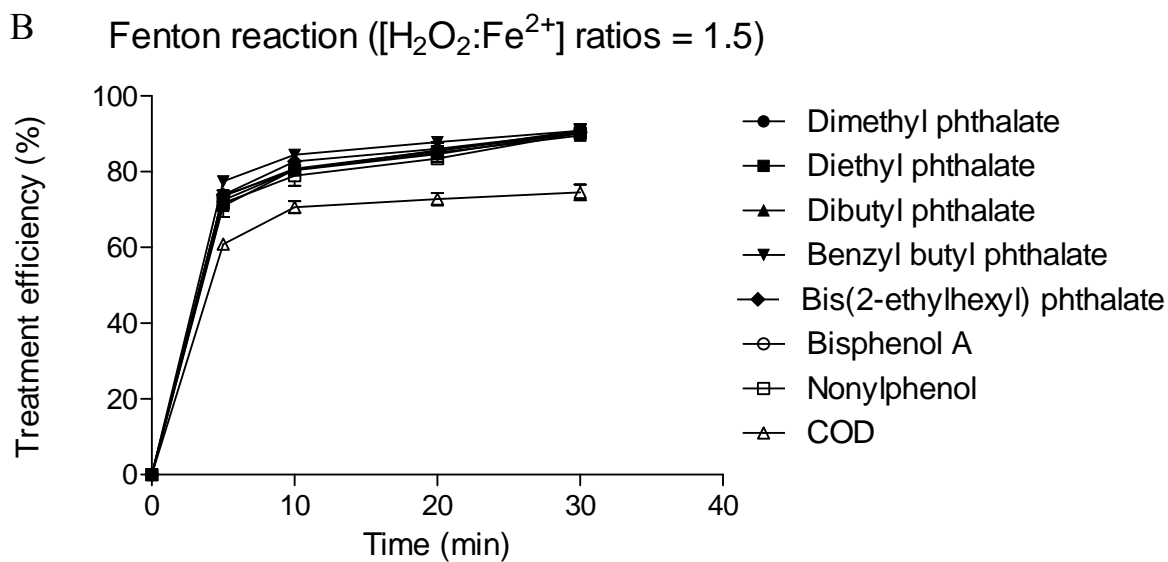
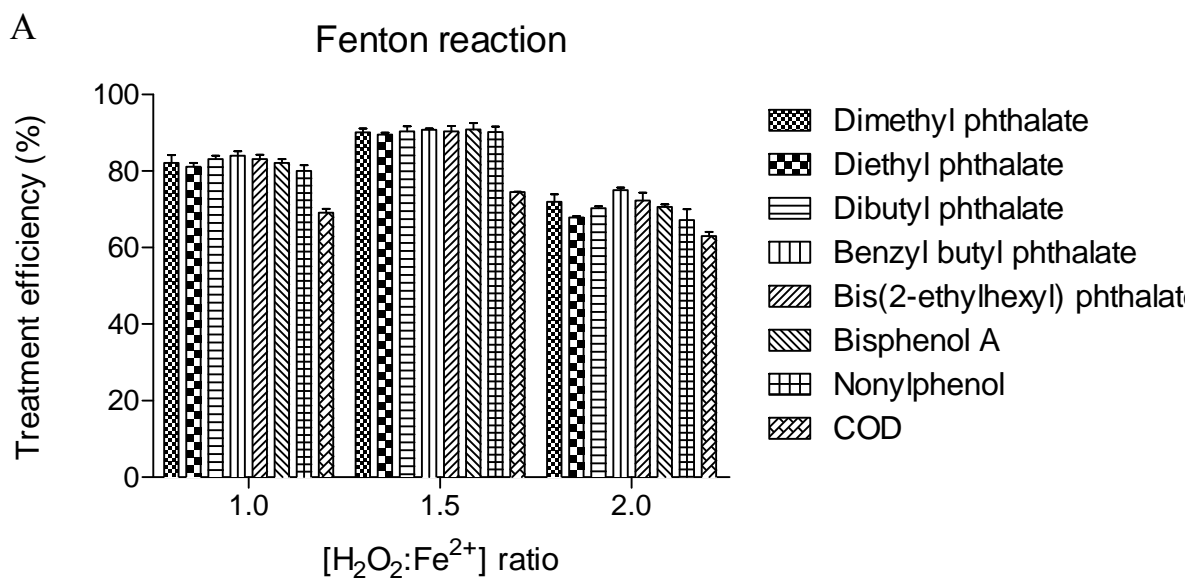


Fig. 4

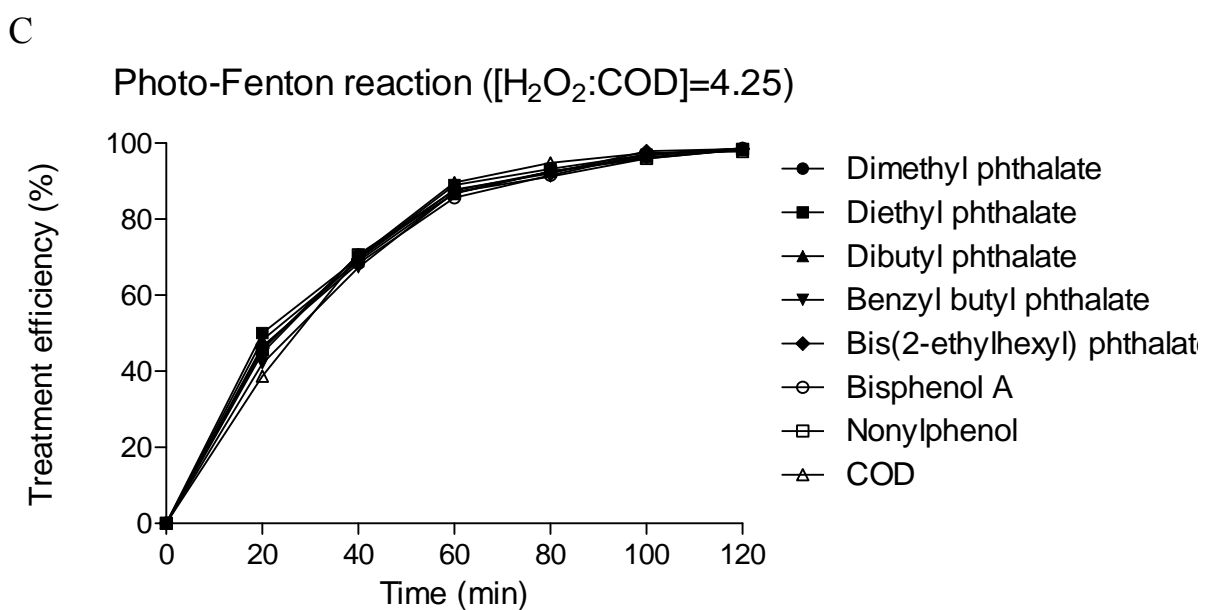
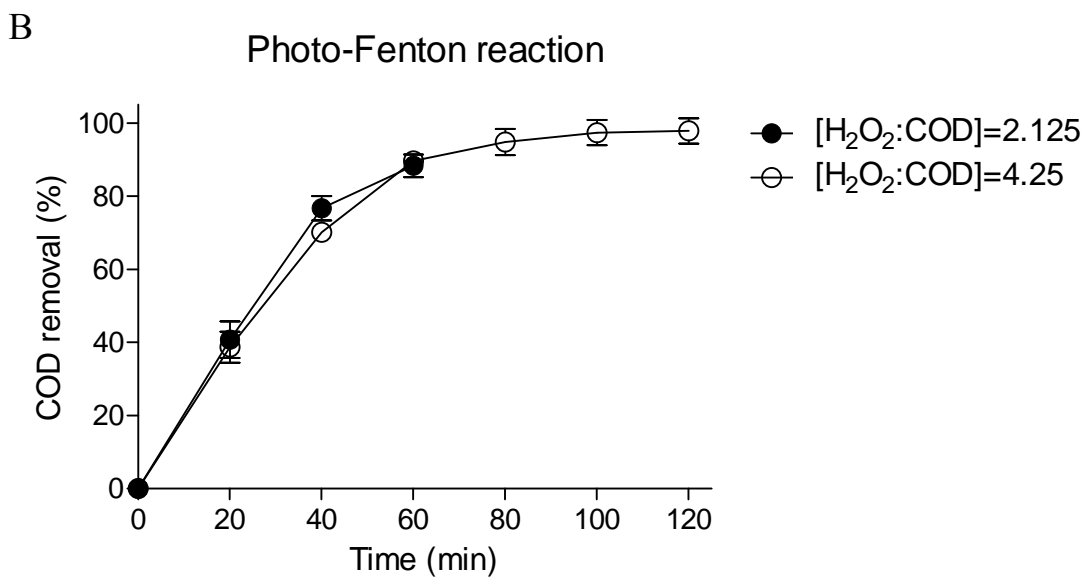
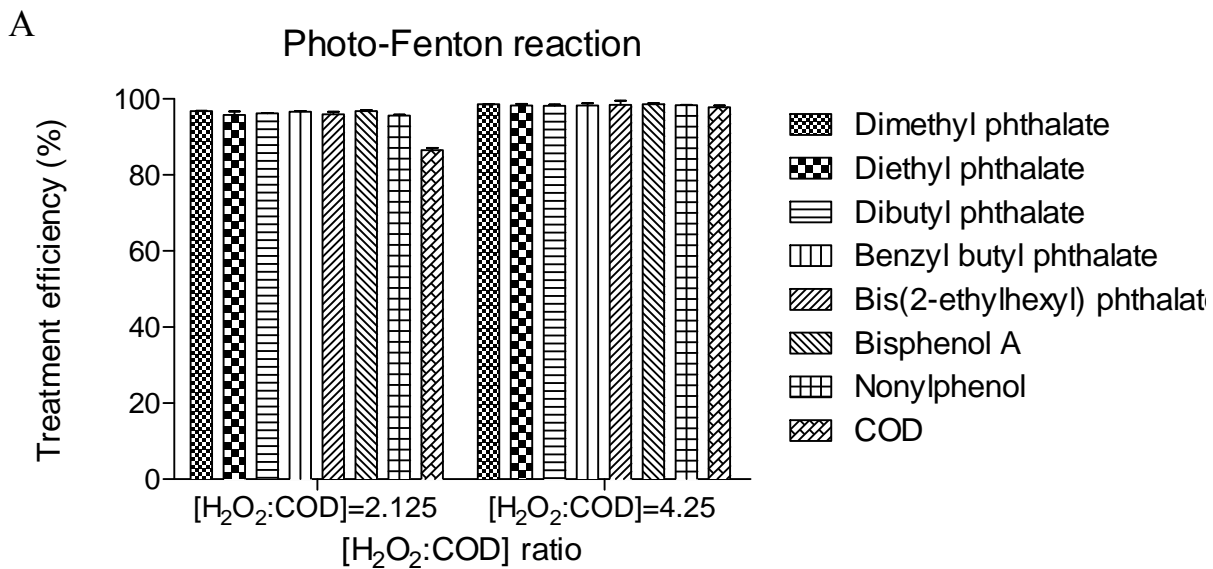


Fig. 5

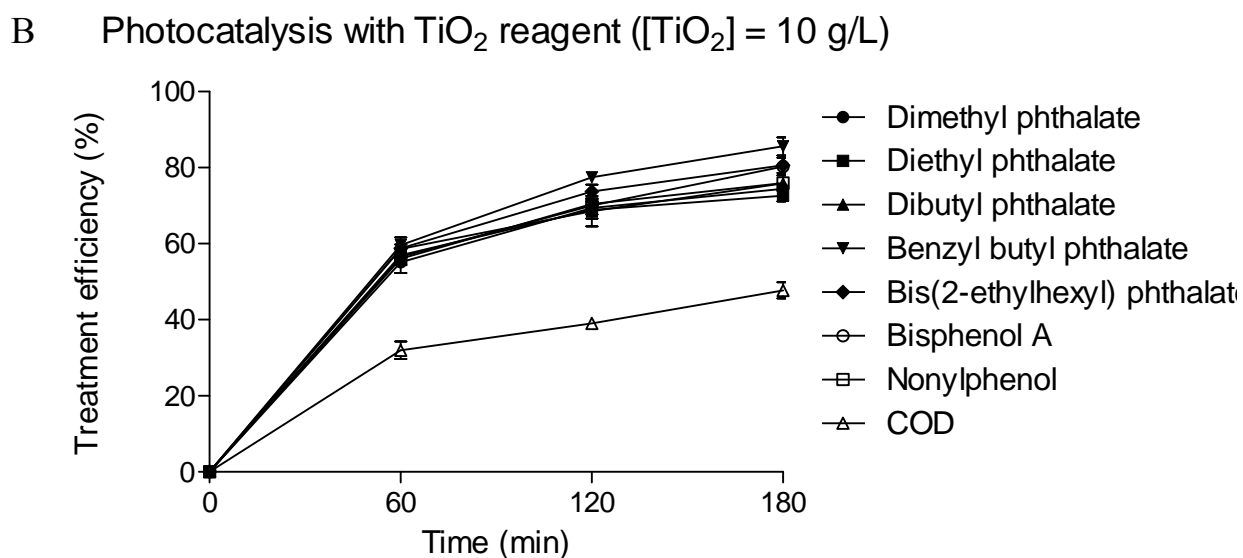
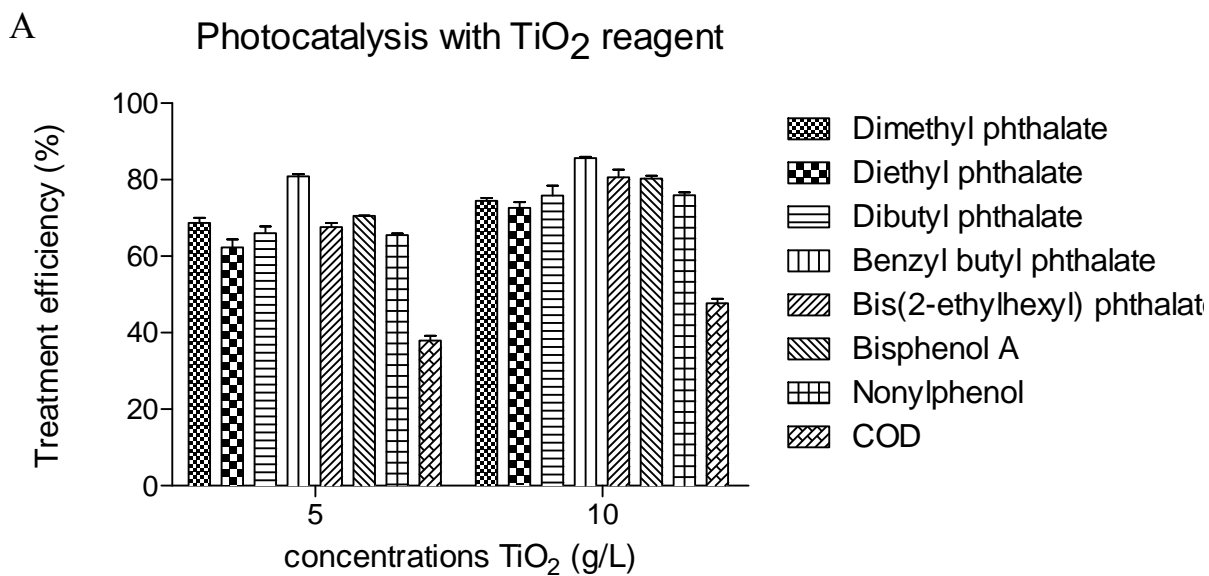


Fig. 6

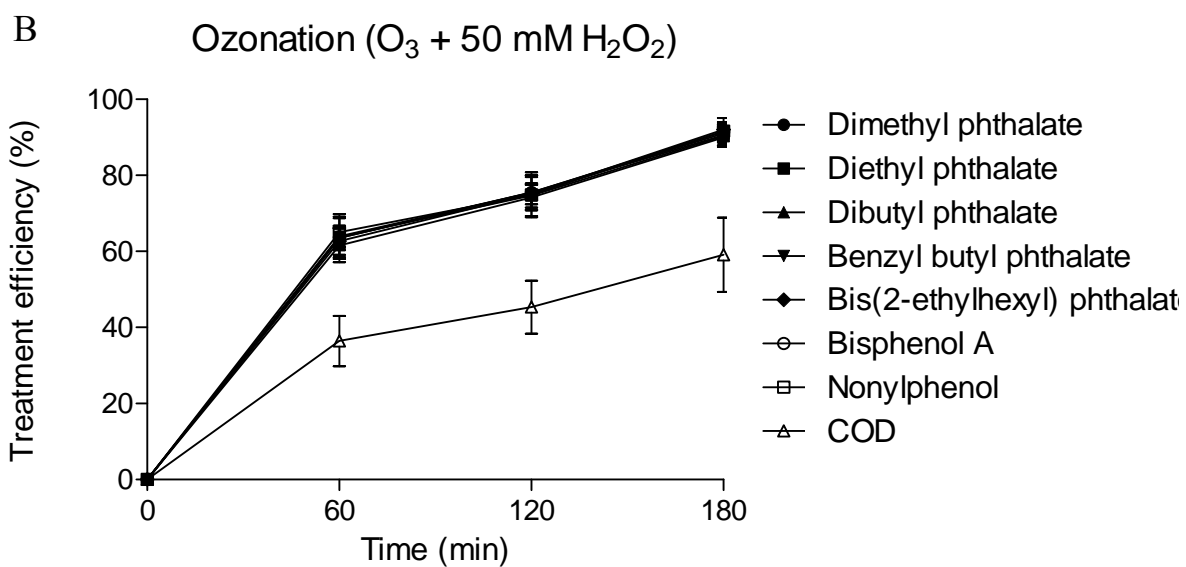
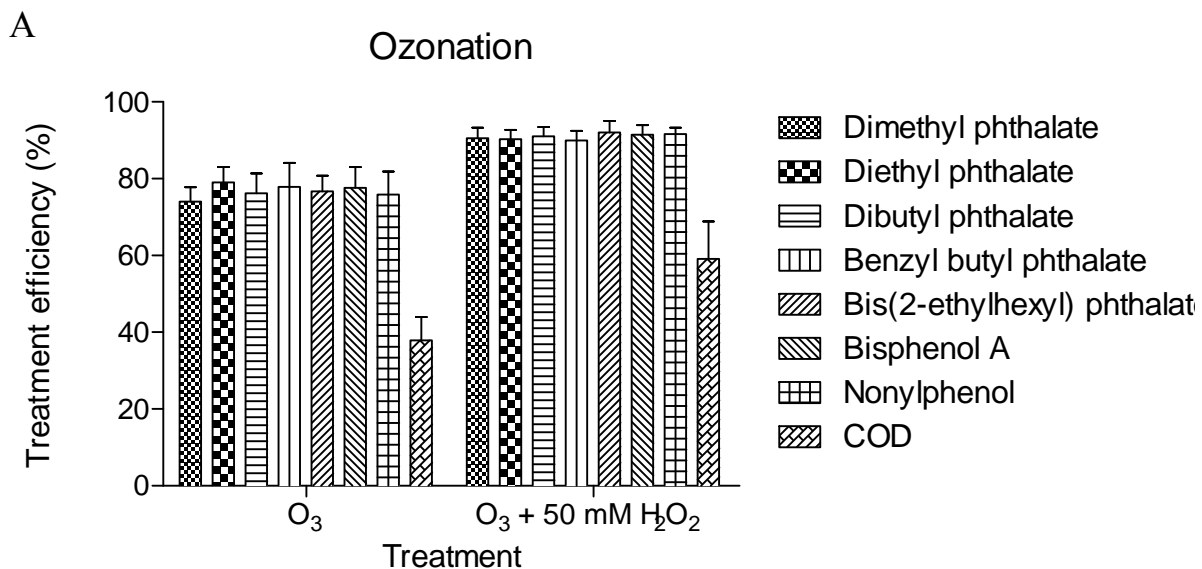


Fig. 7

Table 1. Economical cost assessment of tested advanced oxidation processes at laboratory scale (Fenton process: $[\text{H}_2\text{O}_2] / [\text{Fe}^{2+}] = 1.5$, $[\text{H}_2\text{O}_2] / \text{COD} = 2.125$; Photo-Fenton: $[\text{H}_2\text{O}_2] / [\text{Fe}^{2+}] = 32$ $[\text{H}_2\text{O}_2] / \text{COD} = 2.125$; Photocatalysis: $[\text{TiO}_2] = 10 \text{ g/L}$, time=120 minutes; O_3 : time = 180 minutes; $\text{O}_3 / \text{H}_2\text{O}_2$: $[\text{H}_2\text{O}_2] = 50 \text{ mM}$, time = 180 minutes).

	Fenton	Photo-Fenton	Photocatalysis	$\text{O}_3/\text{H}_2\text{O}_2$	O_3
Energy consumption (kWh)		450	450	540	540
TiO_2 (kg)			1*		
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (kg)	24.31	1.17			
H_2O_2 (kg)	4.46	4.46		1.70	
Coste (€m^3)[†]	10.44	36.26	31.90	38.07	35.64
% COD removal	75	96	39	59	38
$\text{€g COD removal}^{\dagger}$	0.007	0.018	0.039	0.031	0.045

* Considering a10% catalyst replacement.

[†] The price of chemicals was taken from the Chemical Market Reporter; and energy price was 0.066 €/kWh (personal communication from mill managers).