The possibility of removal of endocrine disrupters from paper mill waste waters using anaerobic and aerobic biological treatment, membrane bioreactor, ultra-filtration, reverse osmosis and advanced oxidation processes

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Abstract

An endocrine disrupter is an exogenous agent that interferes with the synthesis, binding, secretion, transport, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and behaviour. Some of them are suspected of causing abnormalities in sperm and increasing hormone-related cancers in humans. Studies have also been published on the estrogen-like responses of endocrine disrupters in wildlife, such as birds, amphibians, reptiles and fish. Endocrine disrupters include a wide variety of pollutants such as alkylphenols, bisphenol A, pesticides, polycyclic aromatic hydrocarbons (PAHs), phthalates, heavy metals, and natural or synthetic hormones. They may be released into the environment in different ways. One of the most important sources of endocrine disrupters are industrial waste waters. The conventional waste water treatment processes are not specifically designed to remove traces of dangerous organic contaminants (except for heavy metals) so the latter are consequently consumed by aquatic organisms and through them may also enter human food chain. In the presented research the following treatments for removing of organic endocrine disrupting

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compounds from paper mill waste waters were compared: anaerobic biological treatment, membrane bioreactor, and reverse osmosis (pilot plant A), and combined (anaerobic and aerobic) biological treatment, ultra-filtration and reverse osmosis (pilot plant B) at pilot scale and advanced oxidation processes (Fenton, photo-Fenton, photo-catalysis with TiO_2 and ozonation) at laboratory scale. The results indicated that the concentrations of organic endocrine compounds from paper mill waste waters were efficiently reduced (100%) by both combinations of pilot plants, photo-Fenton oxidation (95%) while the ozonation, photo-catalysis with TiO_2 reagent and Fenton reaction was less effective (70–80%).

Keywords: endocrine disrupting compounds, anaerobic treatment, aerobic treatment, membrane filtration, advanced oxidation processes, waste water treatment.

1 Introduction

Endocrine disrupting chemicals (EDCs) became the focus of both public and scientific interest when defects in sexual behaviour and reproductive ability of wild-living animals were ascribed to their steroid-like and anti-steroid androgenic properties. These chemicals include different groups of compounds, such as alkylphenol compounds, bisphenol A, dioxins, polyaromatic hydrocarbons (PAHs), polychlorinated bisphenyls (PCBs), phthalates, pesticides, and heavy metals such as cadmium, lead or mercury [1–4]. Environmentally detrimental chemicals with endocrine activity have effect in human health and most of them are mutagenic and highly carcinogenic [5–7].

EDCs may be released into the environment in different ways and one of the most important sources is industrial wastewater. The papermaking industry is not an exception. The pulp and paper industry is the sixth largest polluter, discharging a variety of liquid, solid and gaseous wastes into the environment [8]. The main environmental issues are emissions to water and energy consumption. It is the pollution of water bodies, however, which is of major concern because large volumes of wastewater are generated for each metric ton of paper produced, depending on the raw material, finished product and extent of water reuse. Untreated paper mill effluent discharges cause considerable damage to the receiving waters, since they have high chemical oxygen demand (COD), biochemical oxygen demand (BOD), alkylphenolic and chlorinated compounds, suspended solids (mainly fibres), bisphenol A, phthalates, resin acids, lignin and its derivatives [9–12].

Paper mill effluents will have to be more strictly controlled in order to preserve natural balance in the environment. According to the EU Water Framework Directive 2000/60/EC [13], all industrial water pollution sources will have to be regularly analysed for the content of numerous compounds which are toxic, bio-accumulative or they have function as endocrine disruptors [9, 10]. Consequently, individual producers will be obliged to reduce the impact of their discharges in order to fulfil the requirements of the directive. These necessary steps will ensure better environmental management all around Europe and will also help restore already highly damaged equilibrium of natural surface and underground waters.

Conventional waste water treatment processes are not specifically designed to remove traces of EDCs (except heavy metals), so the latter are consequently consumed by aquatic organisms, and then represent a hazard to the whole food chain. For this reason, it is essential that future research focus on the investigation of appropriate treatment methods that can be integrated into water and waste water treatment facilities to prevent the release of EDCs into the natural waters. Particularly, membrane technologies (ultra-filtration, nano-fitration, and reverse osmosis) and advanced oxidation processes (AOPs) have recently shown promising results in the removal of pollutants from waste waters and surface waters [14].

Activated sludge systems have been successfully applied to treat a wide variety of waste waters, and more than 90% of the municipal and industrial wastewater treatment plants use this treatment type as an important part of their treatment train. Several microorganisms, including bacteria, fungi and yeasts are known for their ability to degrade hydrocarbons to CO_2, H_2O and bacterial cells [15]. Biological treatment, particularly by activated sludge process, has been widely used for the removal of organic compounds from paper mill wastewaters [16].

Membrane filtration technologies, such as ultra-filtration (UF), nano-filtration (NF), and reverse osmosis (RO) have been shown as a promising alternative for removing micro-pollutants [17]. RO will provide and almost complete removal, but the higher implied energy consumption is an important drawback to be considered. Some studies have shown that membrane bioreactors (MBRs) could remove more than 80% of organic potential EDCs from wastewater [18].

There is an increasing interest in utilization of AOPs for destruction of slow degrading compounds. AOPs are based on the production of hydroxyl radicals (OH·) as oxidizing agents to minimize the complex chemicals in the effluents. Fenton reagent (hydrogen peroxide and ferrous iron) is a relatively cheap and easy to operate treatment in comparison to other advanced oxidation processes [19]. Many studies have shown that the oxidising power of Fenton process can be greatly enhanced by combination with the irradiation of UV [20].

Photo-catalysis is another chemical oxidation process in which a metal oxide semiconductor immersed in water and irradiated by near UV light results in the formation of free hydroxyl radical (OH·). TiO_2 is the most widely used catalyst, mainly because of its photo stability, non-toxicity, and water insolubility under most environmental conditions [21].

Ozone can be used for treatment of effluents from various industries [22]. A major disadvantage of the ozonation is the relatively high cost of ozone generation coupled with the short half-life ozone period. Thus, ozone always needs to be generated at site. Some studies indicating that the ozonation was highly efficient for removal organic pollutants and decolorization [16].

The purpose of this study was to investigate, among anaerobic and aerobic biological treatment, membrane filtration trains and AOPs, the most effective method for removing organic endocrine disrupting compounds from a paper mill waste water. Results will provide useful information to industrial applications.

2 Materials and methods

2.1 Material and analytical methods

Effluent samples from a paper mill, before and after every step of the pilot plant A and pilot plant B, were collected in 3L glass bottles. All analyses were made according to the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA and WPCF, 2005) [23]. All chemicals used were of analytical grade.

Organic EDCs were extracted from the samples with use solid phase extraction (SPE) cartridges (Oasis HLB and Strata-X). An Agilent 7890 GC-MS (gas chromatography-mass spectrometry) system with autosampler was used for the determinations of organic EDCs.

Different treatments were compared in their removal efficiency of organic EDCs in the collected wastewater, comprising anaerobic treatment, aerobic treatment, MBR, UF, and RO, at a pilot plant scale, and the following advanced oxidation processes (AOPs) were performed at laboratory scale: Fenton, photo-Fenton, ozonation and photo-catalysis with TiO_2.

2.1.1 Pilot plants treatments

Two pilot plants were installed in the paper mill for the treatment of its waste water flowing out from the dissolved air flotation system placed in the first water loop of the paper mill, which is actually the most contaminated water of the mill.

Pilot plant A consisted of an anaerobic reactor followed by a MBR and a final RO filtration. The effluent of the anaerobic reactor of pilot plant A was discharged into MBR of PES hollow-fibre membranes of 0.05 μm nominal pore size. The water from the MBR entered then into the RO section, formed from spiral wound membranes of polyamide material.

Pilot plant B consisted of a biological double step (anaerobic + aerobic) followed by UF and RO filtration. The effluent of the anaerobic reactor in pilot plant B is discharged into an activated sludge reactor, divided in three successive cascade basins, through where the water flow in series. An aeration system continuously supplied oxygen to the waste water. A secondary sedimentation serves for the separation of the activated sludge from the wastewater coming out from the biological treatments stage. The settled sludge is controlled with a return sludge pumping station which drives it back periodically to the aerobic tank. In this way, the concentration of the activated sludge is kept as constant as possible. The clarified water is then sent to an UF membrane system. UF membranes removed particles greater than 0.04 μm. Finally, the RO unit was formed from membrane modules of spiral wounded polymer with a pore size in the range of 0.1nm. These modules were operated in cross-flow conditions.

2.1.2 AOPs treatments

The same waste water from the paper mill effluent was collected as described above and treated, in the laboratory, evaluating EDCs removal, by the following AOPs: conventional Fenton, photo-Fenton, ozonation and photo-catalysis with TiO_2.

2.1.2.1 Conventional Fento n The experiments were performed in a 3L reactor where 2L of the paper mill waste water were placed and mixed throughout every experiment with a magnetic device. The temperature was adjusted to 20ºC with a water heater and circulator. The pH was continuously and automatically adjusted to 3 (±0.1) along the treatment using 1 $mol \cdot L^{-1}$ sulphuric acid (H_2SO_4) or 1 $mol \cdot L^{-1}$ sodium hydroxide (NaOH). These temperature and pH values are reported to produce best results in the removal of contaminants in waste waters [24]. After temperature and initial pH adjustment, ferrous sulphate ($FeSO_4$) was added to reach the targeted ferrous ion concentration. Five different concentrations of Fe^{2+} were tested, corresponding to $[H_2O_2]:[Fe^{2+}]$ ratios. Hydrogen peroxide (H_2O_2) was then added in batch mode until the designed concentration was reached.

Before the start of the experiment and to the time intervals 20, 40, 60, 80, 100 and 120 minutes, treated water was taken to analysed it. Before extracted with SPE all samples were filtered through a 0.45 μm filter.

2.1.2.2 Photo-Fenton treatment In all these photo-Fenton treatment experiments, the experimental protocol was the same as the one described above for conventional Fenton experiments despite that a 450 W high-pressure mercury immersion lamp was used. This lamp was enclosed inside a quartz glass vessel through which water was circulated in order to reduce the excessive heat generated during the UV irradiation. The lamp was located vertically in the centre of the reactor. The entire assembly was introduced in a safety cabinet.

2.1.2.3 Ozonation The ozonation system included oxygen gas and ozone generator, ozone bubble and trap reactors. The pure oxygen from oxygen generator was allowed to pass into the ozone generator and them the diffuser connecting to the bottom of ozone bubble reactor created bubbles in the ozone reactor filled with paper mill effluent. The ozone flow rate was 4 L/min, with ozone concentration 0.5, 1.5 and 3 ppm. The reaction temperature was 20 °C during all experiments.

2.1.2.4 Photo-catalysis wit h TiO_2 Calculated concentration of TiO_2 was added to the paper mill wastewater and placed into the safety cabinet were the UV light was irradiated with the 450 W lamp described above along 180 min. 200 ml samples were collected and filtered at 0.45 μm every 30 min for measuring EDCs**.**

3 Results and discussion

In our study we found that the combination of biological treatment and membrane filtration are very effective (100%) for removal EDCs from paper mill waste water (Fig. 1-2). RO provided totally removal presented organic EDCs, but the higher implied energy consumption is an important drawback to be considered. The highest removal efficiency of photo-catalysis with TiO_2 reagent, conventional Fenton reaction and ozonation is 70-85% (Fig. 3-5).

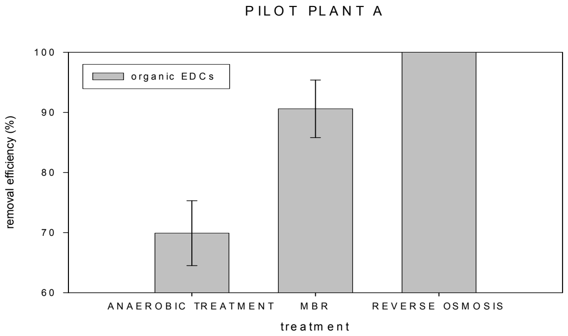

Figure 1: Removal efficiency along the pilot plant A.

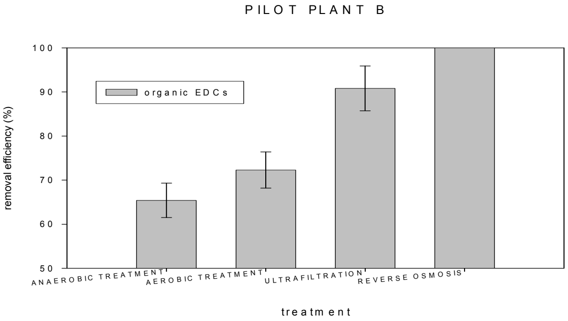

Figure 2: Removal efficiency along the pilot plant B.

Figure 4 shows the EDCs removal efficiency of the performed conventional Fenton treatments to paper mill wastewater, differing on the added concentration of Fe^{2+}. By adding of Fe^{2+}, the removal efficiency of organic substances increased until H_2O_2:Fe^{2+} ratios 2.

Ozone concentration 1.5 ppm with ozone flow rate 4 L/min is enough for 80% EDCs removal from paper mill waste waters (Fig. 5).

Fig. 6 shows that the most effectiveness AOP is photo-Fenton reaction with 95% removal efficiency.

The highest removal efficiency among AOPs was photo-Fenton reaction (Fig. 7).

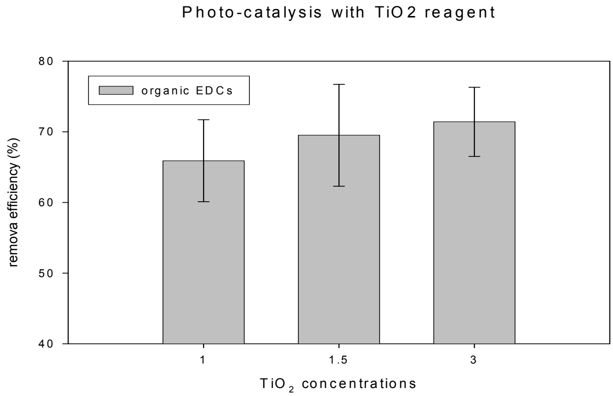

Figure 3: Removal efficiency of photo-catalysis with TiO_2 reagent according the TiO_2 concentrations.

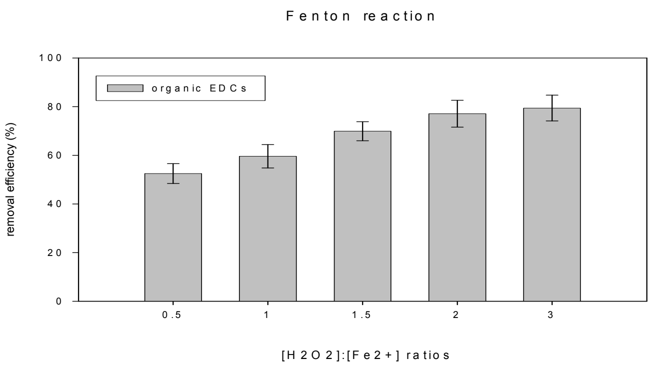

Figure 4: Removal efficiency of conventional Fenton reaction according the H_2O_2:Fe^{2+} ratios.

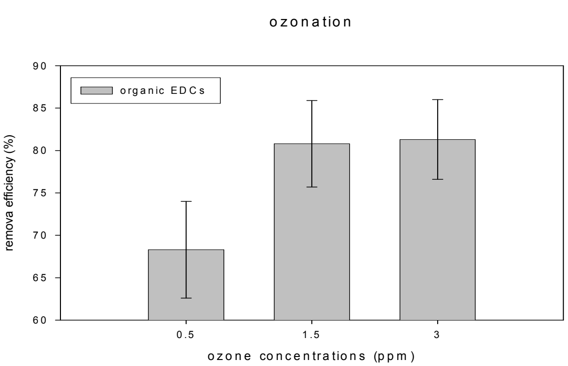

Figure 5: Removal efficiency of ozonation according the ozone concentrations.

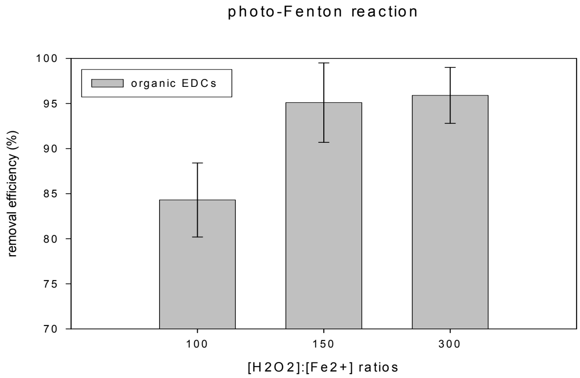

Figure 6: Removal efficiency of photo-Fenton reaction according the H_2O_2:Fe^{2+} ratios.

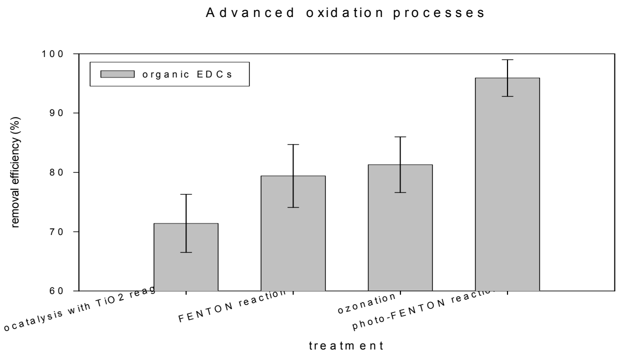

Figure 7: Removal efficiency of AOPs.

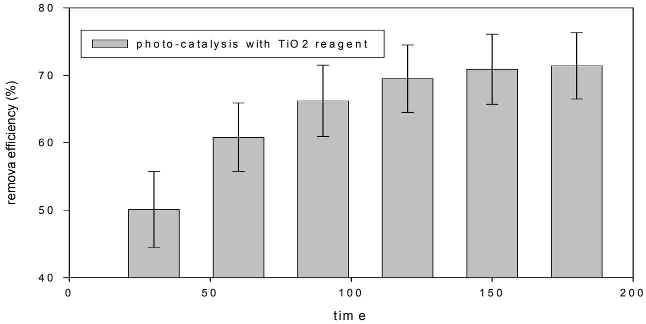

Figure 8: Removal efficiency of photo-catalysis with TiO_2 reagent according to the experiment duration.

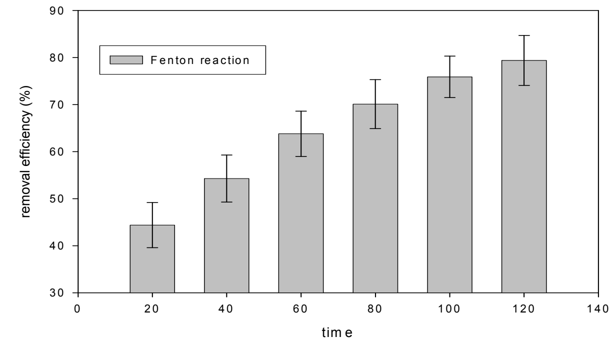

Figure 9: Removal efficiency of Fenton reaction according to the experiment duration.

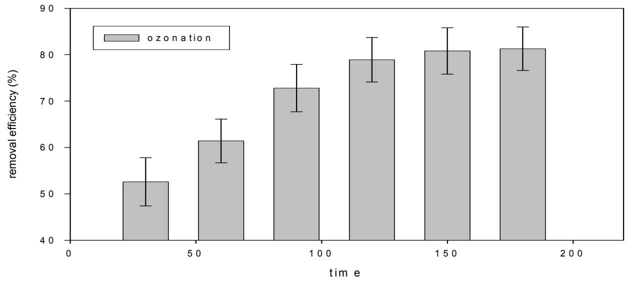

Figure 10: Removal efficiency of ozonation according to the experiment duration.

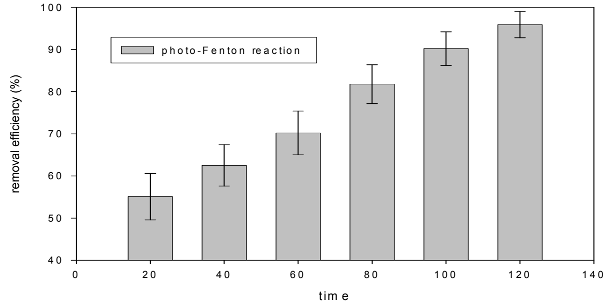

Figure 11: Removal efficiency of photo-Fenton reaction according to the experiment duration.

All experiments with AOPs treatment shows 120 min as enough time to achieve maximum removal effectiveness. (Figs. 8–11).

Figure 7 shows that Fenton reaction has been over a 15% more efficient in the presence of UV light (photo-Fenton reaction). Despite the high efficiency of photo-Fenton reaction, the main disadvantage of this method is the larger power consumption.

4 Conclusions

In the presented study, we investigated different possibilities to remove organic EDCs from the paper mill waste waters. Since some substances present in the paper industry effluents are harmful to the environment and organisms in very low concentrations, such as EDCs, it will be necessary to prevent, or at least limit, their input in the production process; or otherwise perform successful treatments to their removal. Our study shows that the combination of biological treatment and membrane filtration are 100% effective for removal EDCs from paper mill waste water. Reverse osmosis provided totally removal presented organic EDCs, but the higher implied energy consumption is an important disadvantage to be considered. Paper mills are one of the largest industrial consumers of water, and they will have to adopt new technologies of waste water treatment in the future, so they may provide a better water quality, and thus, contribute significantly to a cleaner environment and safer future.

Results showed that among the selected methods of organic contamination treatment of paper mill waste waters, RO, photo-Fenton, and MBR were the most efficient on removing organic EDCs.

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