Treatment by immobilized photocatalysis of timber yard wastewater

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Abstract. Water sprinkling prevents the wood from rotting and becoming infested with insects. This form of storage is largely used in case of severe winter storms during which large quantities of trees can be uprooted (long storage) and in the logging industry for short storage. In both cases wastewater, contaminated by organic substances leached from the wood and the bark, can be discharged to the aquatic environment.

The potential of immobilized photocatalysis to degrade the log preservation wastewater has been evaluated in a falling-film photoreactor, with titanium dioxide immobilised on non-woven paper. Wastewater was produced in a pilot-scale aspersion system in which four wood logs were sprinkled continuously with recycled water for up to six months. The degradation yield after 24hrs (DOC based) varies in function of the wood species: 75% for common beech and 90% for oak.

Keywords: immobilized photocatalysis, titanium dioxide, synchronous fluorescence, UV-visible spectroscopy, wood preservation

1. Introduction

Water sprinkling prevents the wood from rotting and becoming infested with insects. This form of storage is largely used in case of severe winter storms during which large quantities of trees can be uprooted (long storage). In such cases the market is not able to deal with several millions of m^3 of timber. It is necessary to collect as many logs as possible and to preserve their quality as much as possible.

In France, as well as in other countries (Scandinavia for example after the *Per* and *Kyrill* storms in 2007), water sprinkling is largely used. Nowadays the water is continuously recycled but there are still losses toward the environment (soil, water bodies). In the case of large storms the storage can last up to ten years.

Water sprinkling is also used for short storage in timber yards: beech is usually maintained humid in lumber mills to protect the wood from insects and splitting.

In all cases, the wastewater is rich in organic and inorganic matter, which is desorbed from the bark and the wood (Hedmark and Scholz, 2008), Kannepalli *et al*., 2016). However there are only few studies on this type of wastewater. Moreau *et al* (2006) gives values of Chemical Oxygen Demand (COD) around 1500 to 200 mg/L with a very low biodegradability (BOD_5/COD ≈ 0.1-0.5 where BOD_5 is the Biological Oxygen Demand on five days). Kinetics are complex as desorption from the log is combined with biological reactions (on the wood surface as well as in the wastewater) (Borga *et al*., 1996) and abiotic transformations (photolysis under sunlight). The ecotoxicity of limber yard wastewater against *Artemia sauna* and *Vibrio fisheri* has been demonstrated (Svensson *et al*., 2012).

Advance oxidation processes (AOP) have often being proposed for the destruction of organic micropollutants (Reddy *et al*., 2016). In this contribution we proposed to evaluate the possibility to treat timber yard wastewater by photocatalysis on immobilized titanium dioxide.

2. Materials and methods

2.1. Wastewater

A pilot scale sprinkling system has been built to produce the wastewater (Figure 1). Four logs (diameter ≈ 20 cm, length ≈ 1 m) are placed in the reactor. Four tree species has been tested: oak (*Quercus*), Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*). Sprinkling has been run for six months. Wastewater was collected in the storage tank at the end of the experiment.

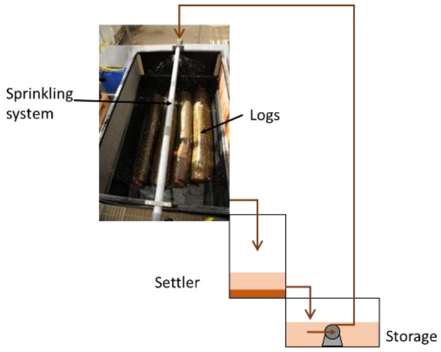

Figure 1. Pilot scale sprinkling system

2.2. Photocatalysis

The photocatalytic tests were performed in a lab-built reactor (Figure 2) made out of stainless steel with a 30×30 cm2 workable area (Fig. 1). The solution to be treated was falling as a thin film from the top of the chamber onto titanium dioxide (Millenium—PC 500, >97 % anatase) immobilized by means of a silica-based binder on a mat made of cellulose fibers (Ahlstrom, Pont-Evêque, France).

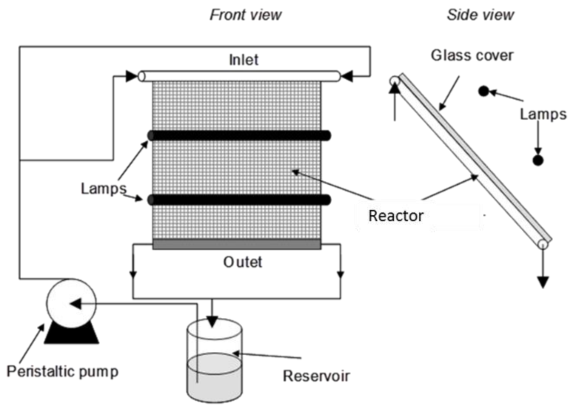

Figure 2. Photocatalytic reactor

The reacting chamber was covered by a transparent glass sheet to avoid evaporation of the solution. The sample (initial volume=500 mL) to be treated was stored in a reservoir and was continuously circulated in the system by a peristaltic pump at a constant flow rate of 200 mL/min. Artificial irradiation was provided by two UV lamps (F15T8, BLB 15W, Duke, Essen, Germany) emitting around 365 nm, positioned parallel to the reactor.

2.3. Analytical methods

Dissolved organic carbon (DOC) and total dissolved nitrogen (TN) have been analyzed on a VCSN device (Shimadzu, Noisiel, France). The Hach method 8000 has been used for COD analysis. UV visible spectra were collected on a UV-visible spectrophotometer (Anthélie Light, Domont, France) between 200 and 600 nm using a quartz cuvette. Synchronous fluorescence spectra have been collected on a Hitachi FL-2500 device (Hitachi, Krefel, Germany) using PMMA cuvettes, with a gap of 50 nm between excitation (scanned between 230 and 600 nm) and emission. **Results**

3.1. Photolysis

Figure 3 summarizes the results obtained by photolysis, i.e. with both lamp on but no photocatalyst in the reactor. Some degradation is observed but it is very limited. However it confirms that over very long period of time, photolysis can occur in full-size sprinkling systems.

3.2. Photocatalysis

As shown in Figure 4, the degradation by photocatalysis is quasi-total (99%) in less than 24hrs, but in all cases residual DOC is observed (≈ 15 mgC/L) (Figure 5). Only a fraction of the nitrogen (≈15%). In photocatalysis organic nitrogen is often only partially transformed into N_2. If another part of organic nitrogen is transformed into ammonium and nitrates, these species remain in solution and contribute to total nitrogen (Khataee *et al.*, 2008; Elmolla and Chaudhuri, 2010; Deletze *et al*;, 2016; Berberidou *et al.*, 2017)

The UV-visible and synchronous fluorescence spectra collected during Scots pine photocatalysis are presented in Figure 6. With respect to the initial UV-visible spectrum at t = 0, no new absorption band are observed during the photocatalysis, that could be related to by-products. Two peaks can be seen on the synchronous fluorescence spectra. The λ_{exc}=280 nm peak corresponds to what is classically called tryptophan-like or protein-like fluorescence. It is due to the indole group, which can have a biological (Coble, 1996) or a vegetal (Roussel, 1974) origin. The λ_{exc}=355 nm peak corresponds to humic substances. Both peaks decreases and the shoulder (λ_{exc}≈400 nm) disappears.

In the synchronous fluorescence spectra observed during photocatalysis of beech and Norway spruce wastewater, a decrease of the humic substances is observed (Figure 7) but the indole peak increases: this is due to the decrease of the wastewater absorbance (Figure 8), which hinders the fluorescence in strongly colored solutions.

3. Conclusions

Immobilized photocatalysis has been tested for the treatment of timber yard wastewater from water sprinkling. The feasibility has been demonstrated with a strong decrease of the carbonaceous pollution (COD, DOC). The experiments should be complemented by toxicity tests to verify the harmlessness of the treated wastewater with respect to the aquatic environment. The process is actually be tested for other timber species.

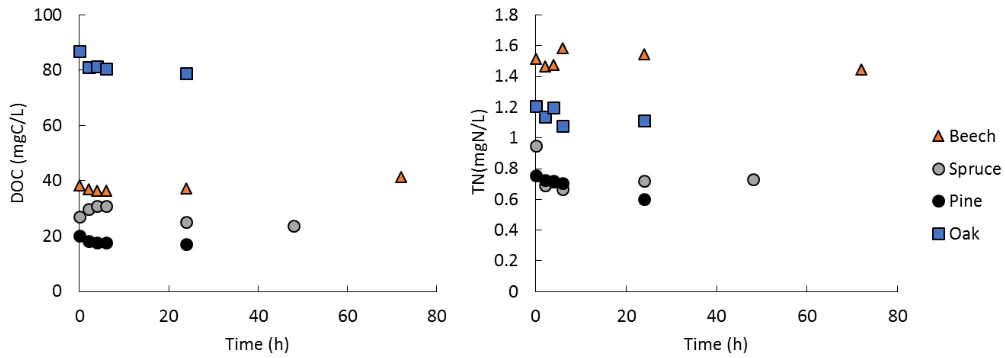

Figure 3. Degradation of dissolved organic carbon and total dissolved nitrogen by photolysis

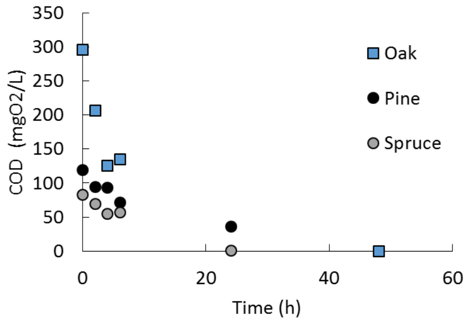

Figure 4: Degradation by photocatalysis, in terms of COD, for oak, pine and spruce

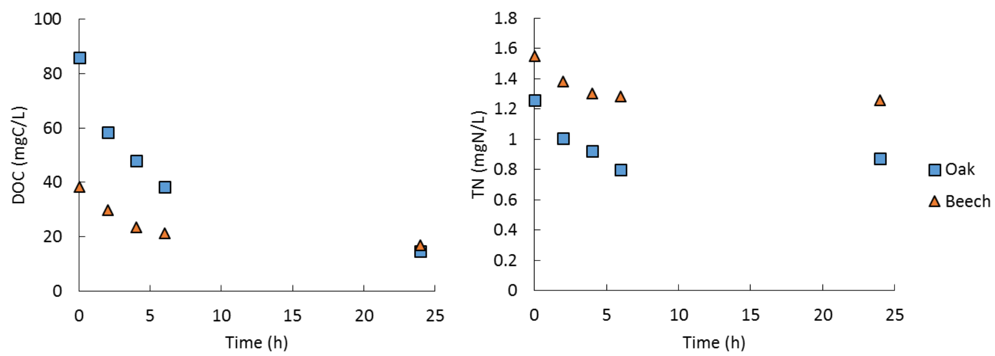

Figure 5. Degradation by photocatalysis, in terms of DOC and TN, for oak and beech

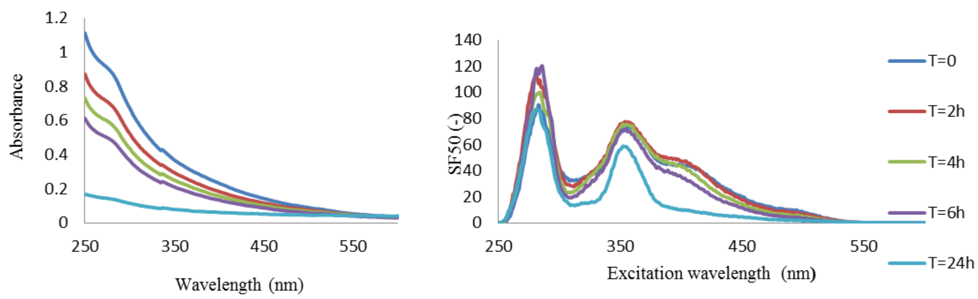

Figure 6. UV-visible spectra (left) and synchronous fluorescence spectra (right) for Scots pine

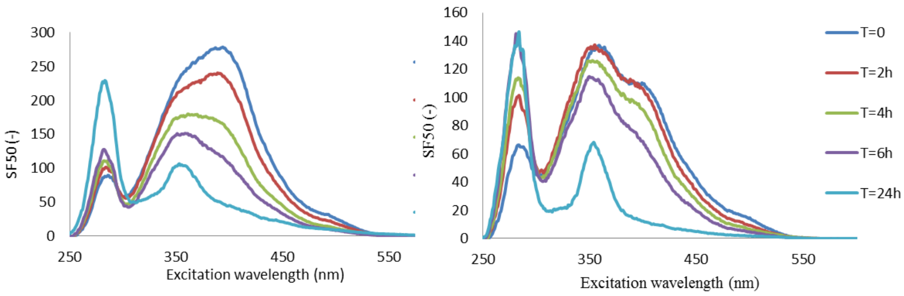

Figure 7. Synchronous fluorescence spectra during photocatalysis for beech (left) and spruce (right)

Figure 8. Decolorization during photocatalysis for spruce

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