# Treatment of Tannery Waste Waters Using Photocatalytic Process with Nanomolecular Materials

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**Abstract:** In this paper, $TiO_2$-photocatalysis was applied to tannery wastewaters from a biologically wastewater treatment plant in order to investigate the technical feasibility of this technology as tertiary treatment. $TiO_2$ nanomolecular supported on different kind of materials were used as catalysts. Preliminary experiments have been performed on laboratory scale using various typologies of nanoparticellar materials coupled with UV light and in aqueous dispersion both in acid and in alkaline conditions. The efficiency of the system has been determined in terms of chemical oxygen demand (COD) reduction.

**Keywords:** Titanium dioxide; photocatalytic process; tannery wastewater treatment

## 1 Introduction

The tannery wastewaters purification is still today a theme of a large interest. Nowadays, treatment depuration technologies allow to obtain effluents with chemical-physical characteristics in respect to the environmental existing rules. From the traditional wastewaters treatments, huge amounts of sewage sludge are generated. In particular, after the biological treatment wastewaters still contain organic pollutants not biodegradable, noted as bio-recalcitrant organic compounds (BROC). These pollutants agents are removed using chemical-physical processes that produce large quantity of sludge. To reduce the production of sludge by these wastewaters tertiary treatments new systems must thus be explored.

The so-called photocatalytic detoxification has been discussed as a promising technology for the wastewater treatment in the scientific literature since 1976 [1]. Photocatalysis is considered an effective system for the mineralization of many organics through the generation of radicals such as $^{\bullet}OH$ and $O_2^{-\bullet}$, reducing considerably the organic load of effluents.

Titanium dioxide, $TiO_2$, is the most widely used semiconductor for photocatalytic studies and applications[2-7] because of its no toxicity, chemical inertness, low costs and capacity to catalyze phenomena of oxidative degradation under the effect of the UV radiation.

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The titanium dioxide has the typical semiconductor electronic configuration with is characterized by a filled valence band and an empty conduction band divided by an energetic gap. Absorption of a photon with an energy $h\nu$ greater or equal than the bandgap energy generally leads to the formation of an electron/hole pair in the semiconductor particle. If a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur. The valence band holes are powerful oxidants (+ 3.5 V vs NHE for $TiO_2$), while the conduction band electrons are good reductans (+0.5 V vs NHE) [8]. Most organic photodegradation reactions utilize the oxidizing power of the holes. The oxidative degradation process goes on through two initial steps that generate free radicals •OH which attack the organic molecules degrading in $CO_2$ and $H_2O$. Fig. 1 shows schematically the mechanism of photocatalysis. The essential reactive species are oxygen as anions $OH^-$ which behave respectively as electron attractor and electron donator, acquiring and giving only one electron, which then goes to regenerate $TiO_2$.

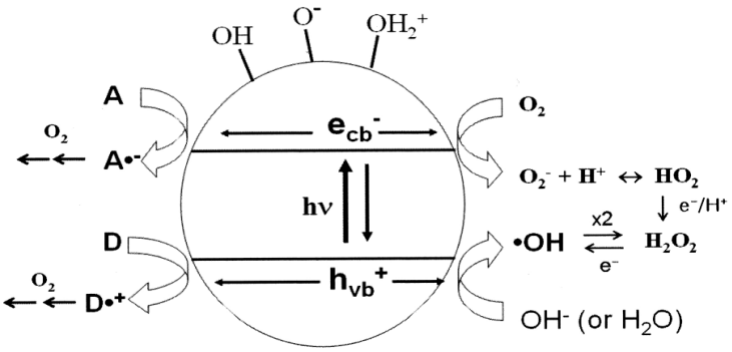


**Figure 1 Principle mechanism of photocatalysis**

The aim of the present study was to investigate the technical feasibility of photocatalysis as tertiary treatment of wastewaters from a centralised tannery wastewater treatment plant located in Santa Croce sull'Arno-Pisa (Italy). Several experimental activities have been performed on laboratory scale using $TiO_2$-nanoparticles supported on glass spheres as catalysts coupled with UV light. The efficiency of the system used has been determined by measuring COD and the concentration of $Cl^-$ ions before and after treatment.

## 2 Experimental

A laboratory cylindrical photoreactor was used in the study as illustrated in Figure 1. The reactor with an effective volume of 1.65 L was filled (fractional voidage of bed = 0.6) with $TiO_2$ supported on glass microspheres (Ø = 1.49 mm) and surrounded with a cooling jacket to maintain a constant temperature of 25°C. The irradiation in the photoreactor was produced by a xenon lamp, positioned in a quartz sleeve and immersed in the solution in the center of the reactor with a main emission of 600 nm.

The experiments were performed in a batch mode by recycling the wastewater (1 L) between a tank and the photoreactor by a centrifugal pump for 4 h.

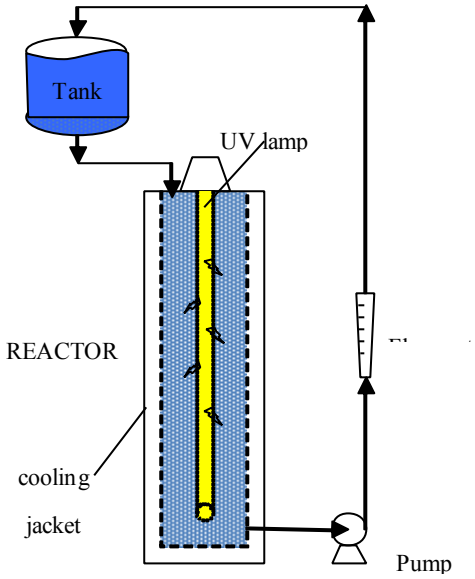


**Figure 2 Scheme of the experimental apparatus used in this study**

All the tests were carried out on tannery wastewater coming from a traditional biological treatment plant and were lasted up to 4 h.

Another important parameter that indirectly gives an efficiency measure of the system is the concentration of chlorides, since the oxidative degradation of the chlorinated substances leads to the formation of $Cl^-$ ions. COD, pH and the concentration of chloride ions were measured before and after the treatment. COD was determined by the proper digestion of the samples (2 h at 150°C) and latter titration with an aqueous solution of $[Fe(NH_4)_2(SO_4)_2]6H_2O$ and $Cl^-$ ions were analyzed by selective electrodes.

## 3 Results and Conclusions

Table 1 shows the different parameters before and after photocatalytic treatment of 4 h.

**Table 1 Results after 4 h of photocatalysis**

| **Run** | **1** | | **2** | | **3** | |
|---|---|---|---|---|---|---|
| Parameter | *Before* | *After* | *Before* | *After* | *Before* | *After* |
| pH | 7.88 | 8.01 | 7.90 | 8.10 | 7.60 | 7.82 |
| COD (mg/L) | 565 | 455 | 450 | 427 | 464 | 448 |
| COD filtrate* (mg/L) | 472 | 460 | 387 | 374 | 358 | 337 |
| $Cl^-$ (mg/L) | 3306 | 3400 | 3380 | 3400 | 3280 | 3320 |

*sample after vacuum filtration on nitrocellulose with pores of 0.45 $\mu$m

The results of this preliminary experimentation showed a moderate COD reduction and a small increase of $Cl^-$ concentration.

These results show encouraging outcome, even if not yet sufficient. We have to direct the research to find the optimal conditions to improve the oxidative capability of the system and to maintain the efficiency of the catalyst in time. A solution could be that of increasing the concentration of oxygen by continuous pumping of air into the reactor through air diffusers. In addition, the fixed bed configuration of catalyst particles does not facilitate the process of replacement and renewal of the substrate on the surface of the catalyst. The air-bubbling, from this point of view, could also be advantageous promoting an effective fluidization of the $TiO_2$ microspheres during the photoreaction improving the degradation capacity of the photocatalytic process.

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