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Photocatalytic Treatment of Industrial Wastewaters using Structured Photocatalysts

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Nowadays one of the most significant environmental problems is related to wastewater treatment because the release of pollutants into the environment has posed a risk to natural ecosystems and human health. Therefore, it is necessary to treat wastewater in appropriately way. Three main steps are applied in wastewater treatments that are commonly called preliminary, secondary and tertiary treatment. The preliminary and secondary treatment steps are based on physical and chemical processes. However, in most cases these types of processes are not enough alone. Among tertiary process treatment, compared to the common processes used for wastewater disinfection, new methods without the formation of disinfection by-products have been recently investigated by researchers. In this sense, among advanced oxidation process (AOPs), heterogeneous photocatalysis is a powerful alternative technique to treat polluted water because it is able to mineralize many organic compounds through the generation of hydroxyl radicals thanks to the presence of a semiconductor activated by a light source. For engineering applications, the immobilization of catalyst powders onto a suitable solid inert support is required. In this work, ZnO immobilized on macroscopic polystyrene pellets has been prepared, characterized and studied in the photocatalytic treatment of four wastewaters samples coming from secondary and tertiary processes of wastewater treatment plant by leather industries. The efficiency of the system has been determined by measuring chemical oxygen demand (COD) and total organic carbon (TOC). Photocatalytic results showed in all cases a significant COD and TOC reduction, after 7 h of UV light irradiation.

1. Introduction

Italian tanneries produce a total turnover of about 5 billion euros a year, more than 70% of which is from exports. Clients are from all over the world and come from the sphere of luxury fashion, design, and the automotive industry. Productions focuses almost only on the process of bovine hides (around 80% of the total) and sheep and goats skins (around 20%), mostly destined to fashion goods manufacturers (footwear, bags and clothing), upholstered furniture (sofas, armchairs and furnishing accessories) and car interiors (seats, steering wheels and dashboards). Our customers belong to very diverse product areas. The presence of tanneries with great versatility in terms of craftmanship and others with highly standardised production let the entire “market pyramid” to be served, from the highest line leather goods to lower priced sofas for mass distribution. The districts, where more than 90% of domestic production is centered, represent the great industrial power of the Italian tanning industry. The main district for both production and employment is situated in Veneto region, in the province of Vicenza. It is dedicated in the production of large bovine leather for car interiors, furniture, footwear and leather goods, and this is the place where the industry’s large industrial groups have developed in recent decades. The second tanning zone in terms of production is in Tuscany, located in the area of S.Croce sull’Arno and Ponte a Egola (province of Pisa). Its prestige is linked to the craftmanship of the production, which is mainly targeted at the luxury fashion. Local tanneries work mainly on medium sized calf and bovine leather, some of which are used for producing sole leather. The usual products of the Campania district, which is situated in Solofra (Avellino), nearby Naples, are sheep and goat leather for clothing, footwear and leather goods. Finally, the Lombardy district, that is mainly situated in the Magenta area; it is mostly specialized in the production of sheep and goat leather for the high fashion industry. Yet, its quality features diversify, since they must be restored through a right purification treatment before water goes back to the environment. Almost all the tanneries located in manufacturing districts discharge their wastewater to specialized water treatment plants consortia. Before this happens, one or more preliminary treatments are carried out in-site, to eliminate coarse wastes, and in some cases (if there are separate piping systems), to recover some of water. The efficiency of the wastewater treatment in the districts eliminates nearly 100% of suspended solids, nitrogen, trivalent chromium, and organic loading (COD) from industrial wastewater (Table 1). Purified water goes back to the environment with qualitative characteristics that guarantee it safe reintegration into natural biological cycles.

Table 1: Reduction of Pollutants in Wastewater Treatment Plants

COD	SUSPENDED SOLIDS	CHROME III	TOT. NITROGEN (TKN)
97.3 %	99.4 %	99.4 %	96.6 %

However, wastewater treatment represents the most significant environmental cost, accounting for more than 60%. Water is the matrix in which most of the processes are carried out but is not truly “consumed” in there. From a quantitative standpoint, discharges represent 93% of the water used in the process. As alternative to the actual technologies used for wastewater treatment, advanced oxidation processes (AOPs) may be applied (Deng et al. 2015). In this sense, heterogeneous photocatalysis is a powerful alternative technique to treat polluted water because it is able to mineralize many organic compounds through the generation of hydroxyl radicals thanks to the presence of a semiconductor activated by a light source (Vaiano et al. 2017). For engineering applications, the immobilization of catalyst powders on the surface of a solid inert support has been applied (Vaiano et al. 2018). In this work, a structured photocatalyst realized immobilizing commercial ZnO powders on macroscopic polystyrene pellets has been prepared, characterized and studied in the photocatalytic treatment of four wastewaters coming from secondary and tertiary processes of sewage treatment plants.

2. Experimental

2.1 Synthesis and chemical-physical characterization of the structured photocatalyst

Commercial ZnO powder (provided by Sigma Aldrich) was immobilized on polystyrene (PS) pellets (mean size of 3 × 3 × 4 mm, Sigma Aldrich) using a solvent assisted procedure (Sacco et al.). ZnO powders (2.5 g) were dispersed in 125 mL of acetone and vigorously mixed until to obtain a homogenous dispersion of photocatalyst particles. Thereafter, 50 g of PS pellets were added and maintained in the suspension for 1 min. After the total evaporation of acetone at room temperature, the excess of ZnO particles not immobilized on PS pellets was removed through several cycles in an ultrasonic bath (CEIA-CP104). Before and after the ultrasound treatment, the weight of the treated pellets was evaluated in order to measure the percentage of ZnO deposited on PS surface, which was found to be equal to 2 wt%. Unsupported ZnO, PS support and ZnO/PS photocatalyst were characterized by means of Raman spectroscopy. In detail, Raman spectra were obtained at room temperature with a Dispersive Micro Raman (Invia, Renishaw) equipped with 514 nm laser in the range of 250-1900 cm^{-1} Raman shift. Specific surface area (SSA) of the samples was performed using BET method by N_2 adsorption at −196 °C with a Costech Sorptometer 1042 after a pretreatment at 35 °C for 120 min in He flow (99.9990%).

2.2 Photocatalytic apparatus

Photocatalytic tests were carried out in a cylindrical pyrex photoreactor (Figure 1), equipped with a peristaltic pump, an air distributor device (flow rate of 142 $Ncc \cdot min^{-1}$), four UV lamps (Philips, nominal power: 8W each; main emission wavelength: 365 nm) placed around and at the same distance from the external photoreactor surface. The amount of ZnO/PS sample was equal to 50 g and the total volume of treated wastewater was 100 mL. The solution, in which air is continuously bubbled, was left in the dark for 2h in contact with the fixed catalytic bed to allow the achievement of the adsorption/desorption equilibrium of the substances in solution on photocatalyst surface. Subsequently, the UV lamps were simultaneously switched on and photocatalytic reaction started. At regular time intervals, about 3 mL of liquid sample was withdrawn from the photoreactor and then analyzed to monitor the reaction progress in terms of residual chemical oxygen demand (COD) and total organic carbon (TOC).

TOC was measured by the high temperature combustion method on a catalyst (Pt-Al_2O_3) in a tubular flow microreactor operating at 680°C, and fed with a stream of air in order to oxidize the organic carbon to CO_2.
It is worthwhile to underline that the pH of the wastewaters was substantially unmodified to analyse the possibility of operating in a wide pH range (Tables 2-5) using the developed photocatalyst. The photocatalytic system was used to treat four different waters (named WW1, WW2, WW3 and WW4) coming from wastewater treatment plant by leather industries. The treated wastewaters are characterized by a brown colour, a slight turbidity and a density and viscosity similar to water.

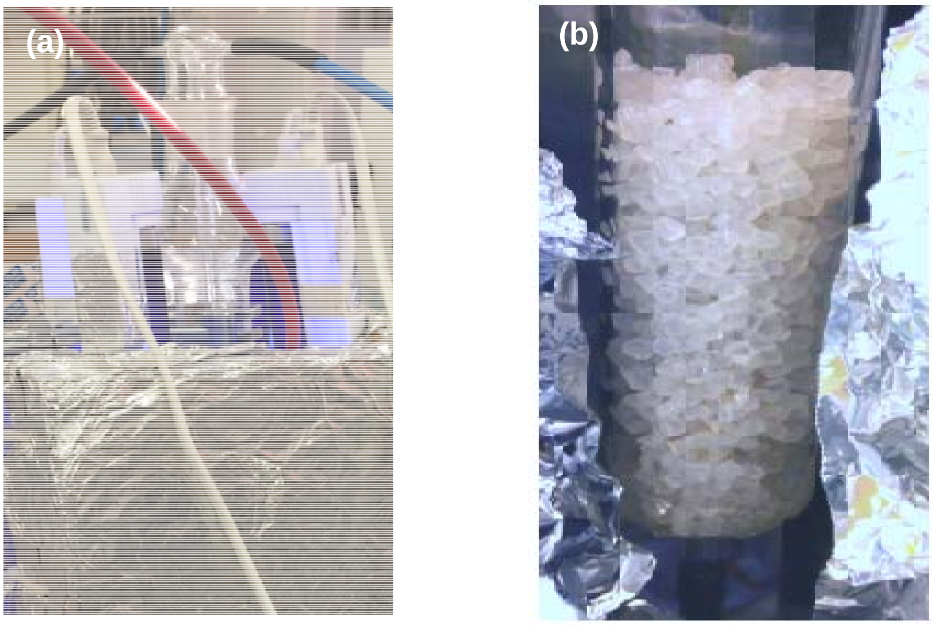

Figure 1: Cylindrical pyrex photoreactor surrounded by the UV lamps (a) and filled with ZnO/PS structured photocatalyst (b)

Table 2: Reduction of Pollutants in WW1

	Wastewater	Wastewater after photocatalytic treatment	Removal (%)
COD (mg L^{-1})	714	187	73.8
pH	7.9	7.9	
TOC (mg L^{-1})	268	51	81.0

Table 3: Reduction of Pollutants in WW2

	Wastewater	Wastewater after photocatalytic treatment	Removal (%)
COD (mg L^{-1})	118	34	71.2
pH	8	8.9	
TOC (mg L^{-1})	50	31	38.0

Table 4: Reduction of Pollutants in WW3

	Wastewater	Wastewater after photocatalytic treatment	Removal (%)
COD (mg L^{-1})	460	328	28.7
pH	8	8.1	
TOC (mg L^{-1})	172	73	57.6

Table 5: Reduction of Pollutants in WW4

	Wastewater	Wastewater after photocatalytic treatment	Removal (%)
COD (mg/L)	160	32	80.0
pH	7.6	7.2	
TOC (mg L^{-1})	60	18	70.0

3. Results

3.1 Raman spectra

Figure 2 shows the Raman spectra relating to the PS support and commercial ZnO in powder form in comparison with ZnO/PS structured photocatalyst in the range 250-1900 cm^{-1}.
PS support displayed main bands at about 621, 1000 and 1600 cm^{-1} due to the Raman active fundamentals modes of polystyrene (Anema et al. 2010). Commercial ZnO in powder form evidenced the presence Raman signals associated to ZnO in wurtzite phase (Zhang et al. 2014). From the comparison of Raman spectra, it can be seen that, for ZnO/PS, the bands corresponding to PS are noted with together the main band related to ZnO at 438 cm^{-1}, as reported in the Raman spectrum of commercial ZnO in powder form. SSA value of PS support was 0.03 m^2 g^{-1}, lower than that achieved for ZnO/PS (0.2 m^2 g-1). These results underline that the adopted synthesis procedure is able to immobilize ZnO powders on the surface of PS pellets.

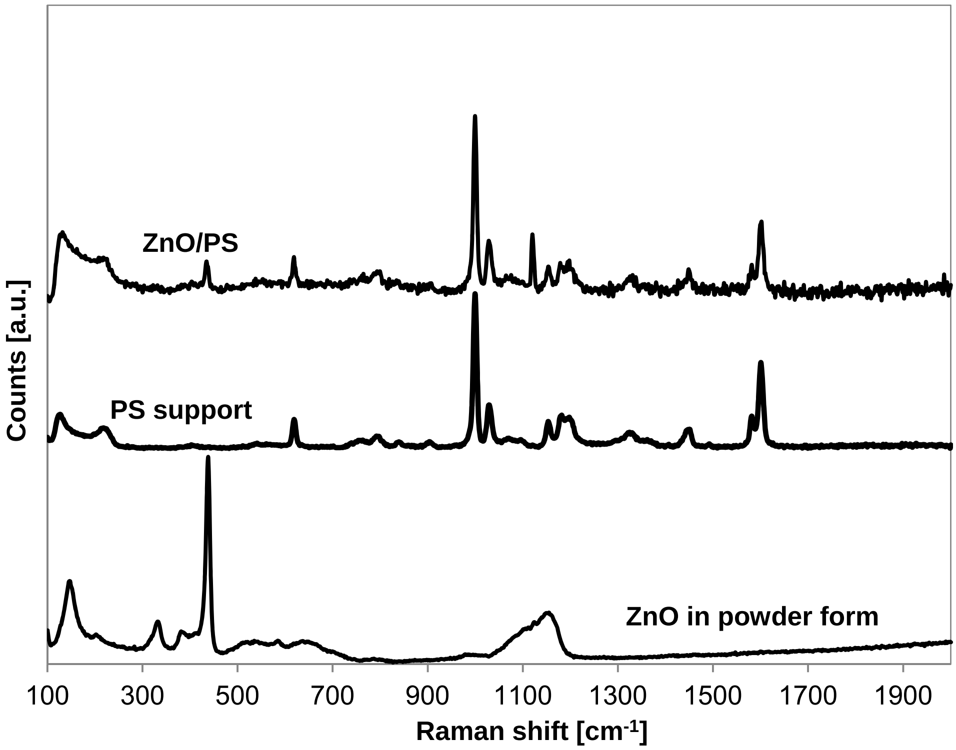

Figure 2: Raman spectra of PS support, commercial ZnO in powder form and ZnO/PS structured photocatalyst

3.2 Photocatalytic activity results

Figure 3 shows the results of the UV photocatalytic tests in terms of TOC/TOC_0 behavior during the test time for WW1. It can be seen that the use of commercial ZnO in powder form (at dosage equal to 9 g L^{-1}) allowed to obtain the almost complete removal of the organic substances while, with ZnO/PS, the TOC removal was about 81% after 7 h of UV irradiation time. Despite the better photocatalytic performance achieved with the commercial ZnO in powder form, the use of ZnO/PS as fixed bed in the photoreactor (Figure 1) allows to avoid the post-treatment step for recovering photocatalyst powder from the treated wastewater, which must be performed when a slurry photocatalytic reactor is used for the removal of water pollutants.

Therefore, from an engineering point of view, the possible use of ZnO/PS can make cheaper the photocatalytic treatment. ZnO/PS was also able to completely decolorize WW1 (Figure 4) and reduce its COD from 268 to 51 mg L^{-1} (Table 2). Similarly, ZnO/PS allowed to reduce both TOC and COD for WW2 (Table 3), WW3 (Table 4) and WW4 (Table 5) after 7 h of UV treatment time. However, further studies are necessary to understand the role of inorganic species present in the wastewater samples treated in this study on the different photocatalytic performances observed for WW1, WW2, WW3 and WW4.

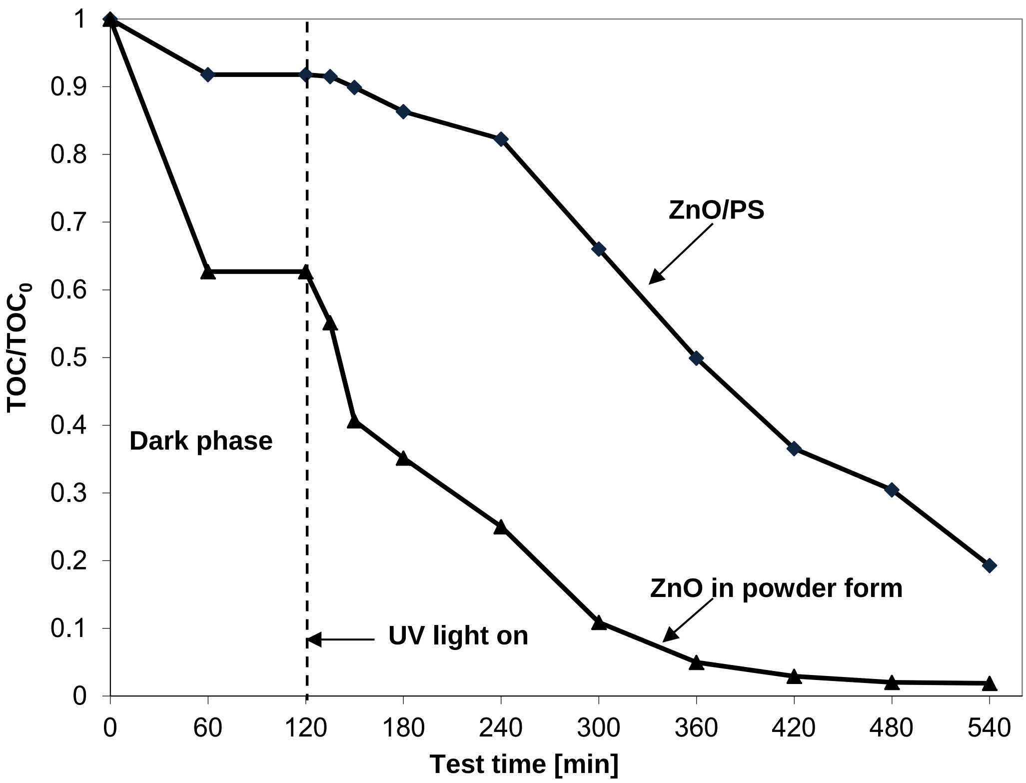

Figure 3: Behavior of TOC/TOC_0 for WW1 as a function of test time for commercial ZnO in powder form and ZnO/PS

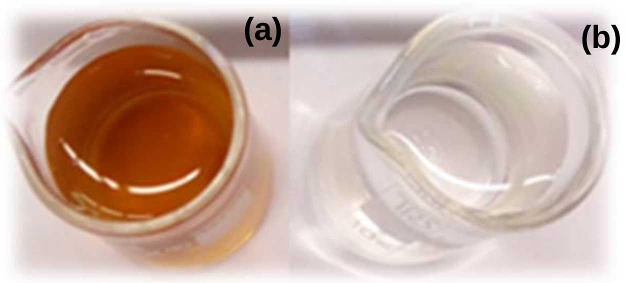

Figure 4: WW1 before (a) and after the photocatalytic treatment (b)

4. Conclusions

The photocatalytic treatment of aqueous samples coming from wastewater plant by leather industries has been studied using ZnO/PS structured catalyst. Raman results showed that ZnO particles were successfully immobilized on PS pellets using a solvent assisted procedure. Photocatalytic tests demonstrated that ZnO/PS photocatalyst was able to assure the reduction of both COD and TOC of four different wastewater samples under UV light irradiation. The obtained results evidenced the efficiency of the synthetized photocatalyst in the treatment of real wastewater coming from leather industries.

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