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Treatment of Dyeing and Finishing Waters Using Innovative Photocatalysts

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Waters coming from dyeing and finishing processes by leather industries produce serious problems because they contain dyes and other pollutants. Toxic and recalcitrant for the environmental, these pollutants are difficult to remove by conventional treatments. For this reason, the heterogeneous photocatalysis is a promising and efficient method to remove them.
ZnO is an excellent and promising photocatalytic material to oxidize organic pollutants into CO_2 and H_2O. In order to enhance the photocatalytic activity of ZnO, in this work, the doping of ZnO with praseodymium (Pr) has been realized and studied in the photocatalytic treatment of dyeing and finishing waters with a total organic carbon (TOC) values in the range 540-1200 $mg \cdot L^{-1}$.
ZnO particles doped with Pr were prepared by a modified precipitation method and characterized by different techniques (XRD, Raman, UV-Vis DRS). The photocatalytic activities of the synthesized samples were investigated under UV light with a specifically photocatalytic apparatus designed for the experimental tests. Photocatalytic results showed a discoloration in the range 56-98% after 4 h of irradiation while TOC removal was about 40% after 3 h of UV irradiation for all the investigated dyeing and finishing waters. The obtained results evidenced the efficiency of the synthetized photocatalyst in the treatment of real dyeing and finishing water coming from leather industries.

1. Introduction

Leather industries are one of the biggest polluters in the world due to the complex nature of their discharged waters. During the production of the skin, a multitude of chemicals and a large quantities of water are used to convert raw skins into leather and so, large volumes of water are generated. These waters constitute one of the main sources of environmental pollution due to the high value of the chemical oxygen demand (COD), , a high concentration of heavy metals, strong odour and intense coloration. The consumption of process water, and consequently the water that is discharged, changes significantly raw materials and products involved in the tanning process (Saxena et al., 2017).
In this work, the attention was focused on dyeing and finishing processes in which the discharged water are characterized by a high concentration of total organic carbon (TOC), presence of heavy metals and an intense coloration of discharged water, which highlight the need for environment friendly technologies capable to reduce the pollutant load of the effluents, avoiding both the use of harmful chemicals and the production of by-products to be disposed of (Dixit et al., 2015). To prevent negative impact on the environment during leather production, heterogeneous photocatalysis is an innovative and promising technology used for the removal of pollutants. Even if TiO_2 is the most used semiconductor in photocatalytic applications (Wang and Caruso, 2011), the use of zinc oxide (ZnO) is proving just as valid catalyst and in many cases more photoactive than titania (Vaiano et al., 2015). Moreover, the doping is an effective strategy to enhance the photocatalytic performance of semiconductors, as reported in the scientific literature (Vaiano et al., 2016).

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In particular, the use of zinc oxide doped with rare earths showed interesting results for the degradation of the model solutions containing different types of dyes and in the treatment of wastewater coming from industrial processes for the production of hair dyes (Vaiano et al., 2017).
The present work is focused on the treatment of dyeing and finishing waters through a photocatalytic system using ZnO doped with Pr under UV light irradiation.

2. Experimental

2.1 Synthesis of photocatalysts and their characterization

Undoped and doped ZnO with praseodymium were prepared by a modified precipitation method, (Vaiano et al., 2017) in which $ZnSO_4$ (Aldrich, 99%) was used as the precursor of ZnO while $Pr(NO_3)_3 \cdot 6H_2O$ (Aldrich 99.9%) was used as Pr dopant source. The generated precipitate was centrifuged, washed and calcined at 450°C for 30 min. The synthetized photocatalyst (Pr-ZnO) was characterized by X-ray diffraction analysis (XRD), Raman, and UV–Vis diffuse reflectance spectra (UV–Vis DRS).

2.2 Photocatalytic apparatus

The photocatalytic tests were conducted in a cylindrical pyrex photoreactor coupled with a peristaltic pump, an air distributor device (flow rate of 142 $Ncc \cdot min^{-1}$), four UV lamps (Philips, nominal power at 8W each and main emission peak at 365 nm) arranged at the same distance from the external surface of the photoreactor and the photocatalyst dosage was 3 $g \cdot L^{-1}$ dispersed in 100 mL of dyeing and finishing waters.
The photocatalytic system was used to treat different waters coming from dyeing and finishing processes by leather industries. Chemical characteristics of waters are shown in Table 1.
Pr-ZnO photocatalyst was dispersed in water to be treated and the suspension was left in dark conditions for 120 minutes. After that, the photocatalytic test was conducted up to 240 min. The discoloration of the solutions collected at different test times was analysed by UV–vis spectrophotometer (Evolution 201) considering the absorbance at a specific wavelength. At last, the total organic carbon (TOC) was measured by the high temperature combustion method on a catalyst ($Pt\text{-}Al_2O_3$) in a tubular flow microreactor operated at 680°C, with a stream of hydrocarbon free air to oxidize the organic carbon.
It is worthwhile to underline that, the pH of the waters was never modified to demonstrate the possibility to operate in a wide pH range (Table 1), through the developed photocatalytic system.

Table 1: Dyeing and finishing waters characteristics

	Dyeing water	Finishing water 1	Finishing water 2
TOC [$mg \cdot L^{-1}$]	452	1205	541
pH	2.3	6.4	6.2
Cd [$mg \cdot L^{-1}$]	<0.005	<0.005	<0.005
Cr [$mg \cdot L^{-1}$]	30	0.25	2.5
Fe [$mg \cdot L^{-1}$]	3.5	1.8	14
Mn [$mg \cdot L^{-1}$]	0.1	0.1	<0.005
Ni [$mg \cdot L^{-1}$]	<0.005	<0.005	<0.005
Pb [$mg \cdot L^{-1}$]	<0.005	<0.005	<0.005
Cu [$mg \cdot L^{-1}$]	0.1	0.04	0.3

3. Experimental results

3.1 Characterization of the photocatalysts

Figure 1a shows the Raman spectra of the undoped ZnO and Pr-ZnO catalyst in the range of 150-750 cm^{-1} in which the main bands related to the zinc oxide were observed.
The XRD patterns of the same photocatalysts (Figure 1b) evidenced five peaks at 2θ=32.06°, 34.74°, 36.53°,47.85° and 56.97°, respectively indexed to the (100), (002), (101), (102) and (110) planes of hexagonal wurtzite crystal structure (Soares et al., 2017) and no signals related to praseodymium oxide (Khataee et al., 2015) were detected, demonstrating the effectiveness of the doping process. Considering the peak at 2θ=36.53°, it was calculated the average crystallite sizes of the samples using the Debye-Sherrer's equation in which the crystallite size value of Pr-ZnO photocatalyst (21 nm) is lower than the undoped ZnO (25 nm).

The UV-Vis DRS spectra, in terms of Kubelka-Munk (KM) of the undoped ZnO and Pr-ZnO photocatalyst is showed in Figure 2. It is evident that the absorption threshold of undoped ZnO sample was at about 390 nm (Figure 2a). It may also be noted a shift of the absorption threshold towards the visible region for the Pr-ZnO photocatalyst (Figure 2a) with a wide absorption band in the range 410-660 nm. As a consequence a slight reduction of the band gap value in comparison to the undoped ZnO has been achieved (Figure 2b).

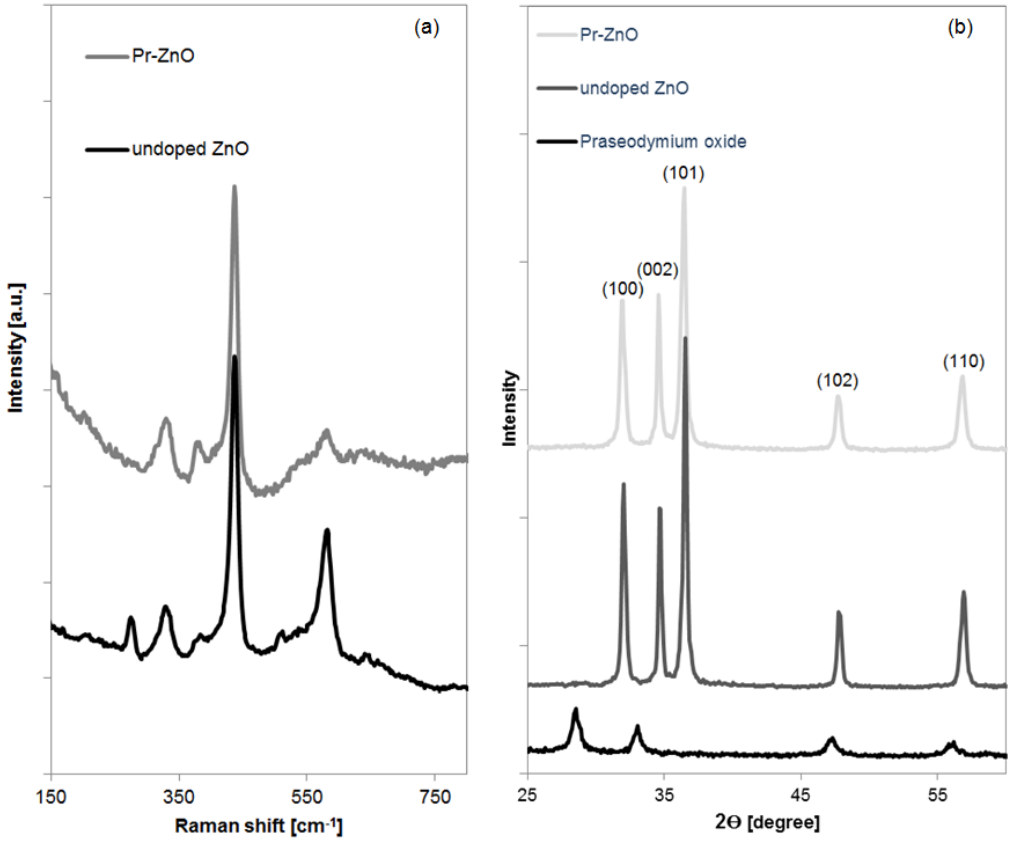

Figure 1: Raman spectra of undoped ZnO and Pr-ZnO photocatalyst (a) and XRD patterns of undoped ZnO, Pr-ZnO photocatalyst and praseodymium oxide (b)

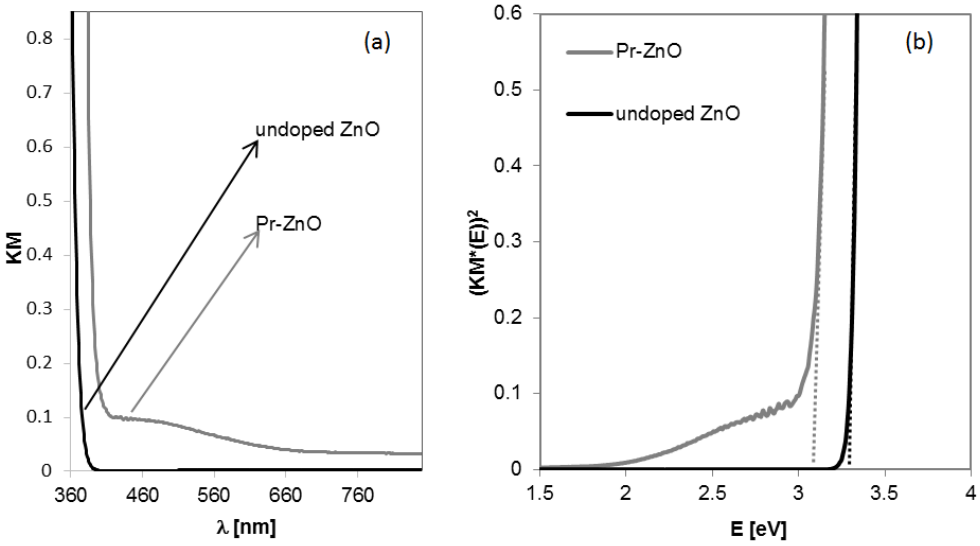

Figure 2: UV-Vis DRS spectra of undoped ZnO and Pr-ZnO photocatalyst as a function of wavelength(a) and band gap energy calculus (b).

3.2 Photocatalytic tests

The photocatalytic experiments were carried out using Pr-ZnO photocatalyst. Figure 3 shows the results in terms of discoloration for dyeing water and finishing waters as a function of run time.
In particular, the discoloration was obtained by monitoring over time the absorbance characteristic of the colour of the treated water. A typical behaviour of the absorbance versus time is shown in Figure 4.

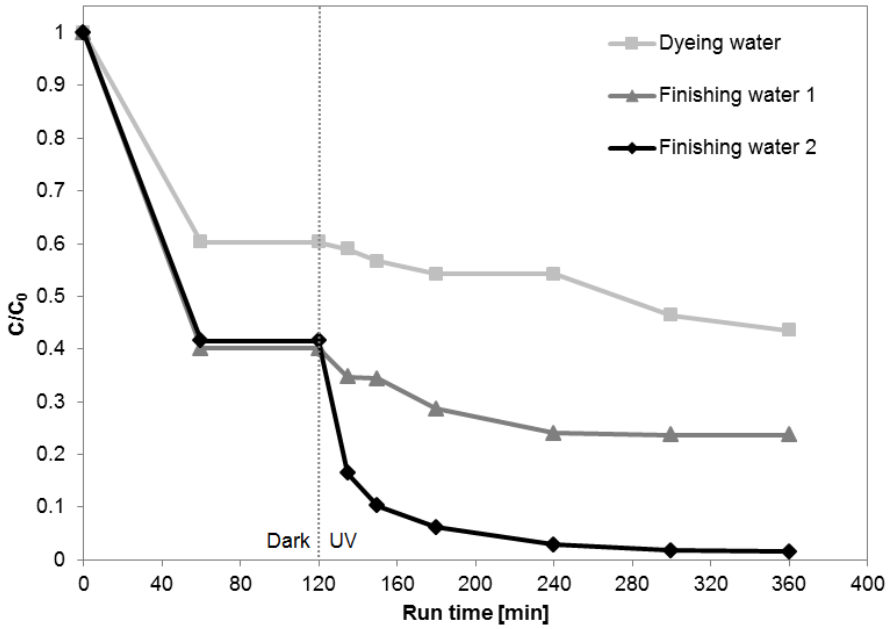

Figure 3: Photocatalytic discoloration of dyeing and finishing waters as a function of run time.

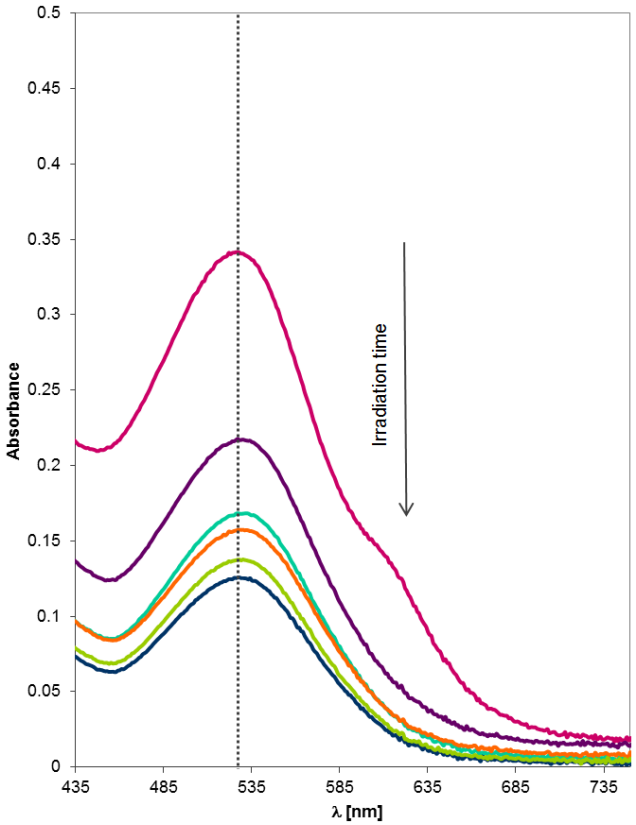

Figure 4: UV-Vis absorbance spectra during the irradiation time for the finishing water 1.

In Figure 3, it is possible to observe that, in dark conditions, the adsorption equilibrium on Pr-ZnO surface is reached in 60 min leading to a discoloration of about 40 and 60% for the dyeing water and finishing waters, respectively. During the irradiation time, Pr-ZnO photocatalyst allowed to obtain 54 and 76% for the dyeing and finishing water 1, respectively, after 240 min under UV light (Figure 3). As regards to finishing water 2, it was obtained the almost complete discoloration in 240 min of UV irradiation (Figure 3).
Figure 5a reports the discoloration degree and TOC removal values after 180 min of test time for all the treated waters. In particular, it was obtained a discoloration degree of about 56, 76 and 98% for dyeing water, finishing water 1 and 2, respectively, while TOC removal was about 40% for all the treated waters. Possibly, the lower value of TOC removal with respect to the discoloration degree is due to the presence of colourless organic substances that are more difficult to degrade.
The discoloration of the treated waters is evident from the observation of Figures 5b, 5c and 5d. The obtained results evidenced the efficiency the Pr-ZnO photocatalyst in the treatment of real dyeing and finishing water coming from leather industries.

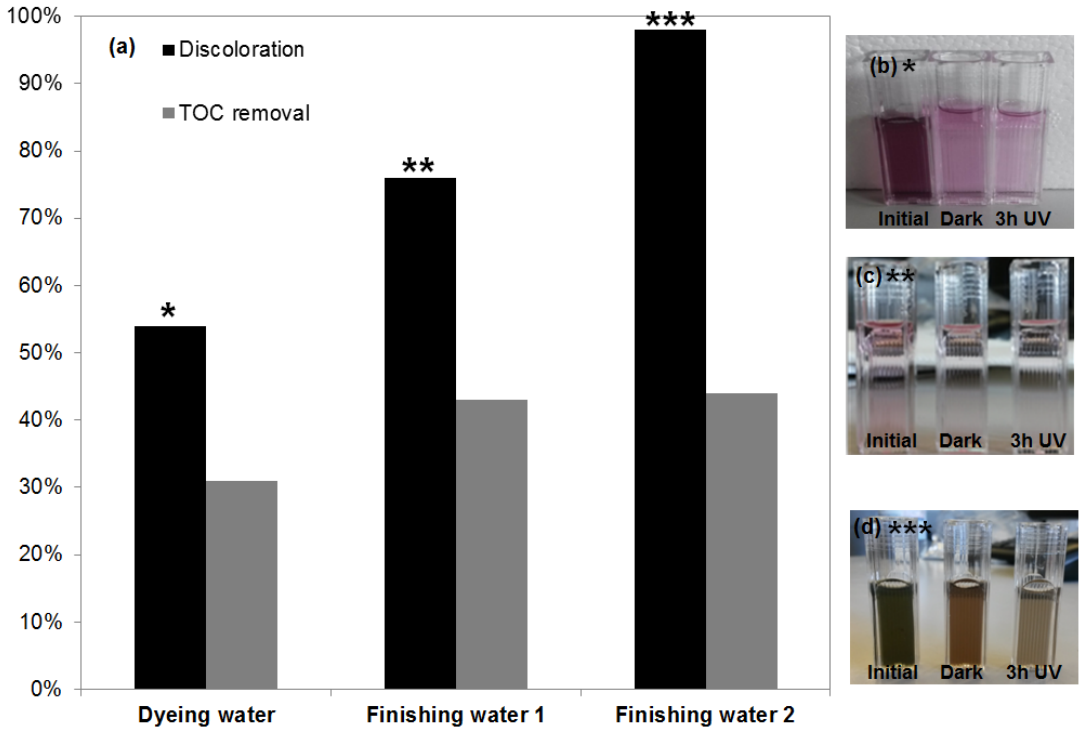

Figure 5: Discoloration and TOC removal of dyeing and finishing waters after 180 min of UV irradiation.

4. Conclusions

The photocatalytic treatment of waters coming from dyeing and finishing processes by leather industries has been studied using Pr-ZnO photocatalyst. Characterization results showed that the Pr doping induced a shift toward the visible region with a slightly decrease of the band gap value in comparison to undoped ZnO photocatalyst. Photocatalytic tests of dyeing and finishing waters demonstrated that Pr-ZnO photocatalyst was able to obtain a discoloration degree higher than 50% after 240 min under UV light with a TOC removal of about 40% after 180 min under UV light irradiation. The obtained results evidenced the efficiency of the synthetized photocatalyst in the treatment of real dyeing and finishing water coming from leather industries.
In general, the photocatalytic process is used in water treatment plants as a tertiary process. Given the complexity of the industrial waters that has been treated here and with respect to the residual values of TOC (2701-723 $mg \cdot L^{-1}$), it can be said that the photocatalytic process can be proposed as a pre-treatment step for other treatment units (such as the biological process) in order to make the treated waters more easily to degrade.

Reference

Dixit, S., Yadav, A., Dwivedi, P. D. & Das, M. 2015. Toxic hazards of leather industry and technologies to combat threat: A review. *Journal of Cleaner Production,* 87**,** 39-49.

Khataee, A., Karimi, A., Arefi-Oskoui, S., Darvishi Cheshmeh Soltani, R., Hanifehpour, Y., Soltani, B. & Joo, S. W. 2015. Sonochemical synthesis of Pr-doped ZnO nanoparticles for sonocatalytic degradation of Acid Red 17. *Ultrasonics Sonochemistry,* 22**,** 371-381.

Saxena, G., Chandra, R. & Bharagava, R. N. 2017. Environmental pollution, toxicity profile and treatment approaches for tannery wastewater and its chemical pollutants. *Reviews of Environmental Contamination and Toxicology.*

Soares, A. F., Tatumi, S. H., Mazzo, T. M., Rocca, R. R. & Courrol, L. C. 2017. Study of morphological and luminescent properties (TL and OSL) of ZnO nanocrystals synthetized by coprecipitation method. *Journal of Luminescence,* 186**,** 135-143.

Vaiano, V., Matarangolo, M., Sacco, O. & Sannino, D. 2017. Photocatalytic treatment of aqueous solutions at high dye concentration using praseodymium-doped ZnO catalysts. *Applied Catalysis B: Environmental,* 209**,** 621-630.

Vaiano, V., Sacco, O., Iervolino, G., Sannino, D., Ciambelli, P., Liguori, R., Bezzeccheri, E. & Rubino, A. 2015. Enhanced visible light photocatalytic activity by up-conversion phosphors modified N-doped TiO_2. *Applied Catalysis B: Environmental,* 176-177**,** 594-600.

Vaiano, V., Sacco, O., Sannino, D. & Ciambelli, P. 2016. N-doped ZnO nanoparticles supported on ZnS based blue phosphors in the photocatalytic removal of eriochrome black-T dye. *Chemical Engineering Transactions.*

Wang, X. & Caruso, R. A. 2011. Enhancing photocatalytic activity of titania materials by using porous structures and the addition of gold nanoparticles. *Journal of Materials Chemistry,* 21**,** 20-28.