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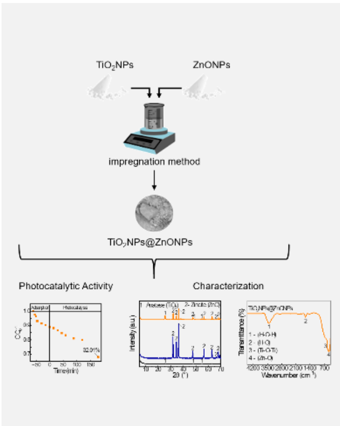
# Bimetallic nanocatalyst with titanium dioxide and zinc oxide nanoparticles: Synthesis, characterization and photocatalytic activity

***R.D. Wouters*[1]*,*** *P.C.L. Muraro*[2]*, G. Pavoski*[3]*, D. C. R. Espinosa*[4]*, W.L. da Silva,*[5]
*(1) Franciscan University (UFN), Santa Maria - RS, Brazil, robson.wouters@ufn.edu.br; (2) Franciscan University (UFN), Santa Maria - RS, Brazil, pamelamuraro@ufn.edu.br; (3) University of the Sao Paulo (USP), São Paulo, SP, Brazil , giovanipavoski@gmail.com ; (4) University of São Paulo (USP), São Paulo, SP, Brazil, espinisa@usp.br; (5) Franciscan University (UFN), Santa Maria - RS, Brazil,* w.silva@ufn.edu.br




Rapid industrial growth, especially in textile industries that result in toxic effects on fauna and flora, has become a serious socio-environmental problem. Simultaneously, the synthesis of nanomaterials using extracts allows for improved properties with fewer environmental effects. Thus, the present study aims to synthesize and characterize a bimetallic nanocatalyst ($TiO_2NPs@ZnONPs$) from natural extracts with titanium dioxide ($TiO_2NPs$) and zinc oxide (ZnONPs) to remove the Rhodamine 6G dye under visible irradiation. $TiO_2NPs@ZnONPs$ presented heterogeneous morphology with a negative surface charge (-14.43 mV), V-type isotherm and H1 hysteresis with $S_{BET}$ = 62.7 m² $g^{-1}$ and Dp = 10.49 nm. The ideal condition was [Rh 6G] = 20 mg $L^{-1}$, [$TiO_2NPs@ZnONPs$] = 1 g $L^{-1}$ and pH = 7 with 32.01 % and the apparent rate of pseudo first-order reaction of $k$ = 0.0027 $min^{-1}$. Therefore, it was possible to synthesize and characterize the bimetallic nanocatalyst for application in the removal of effluents with dyes.

## Introduction

The contamination of wastewater by organic pollutants has emerged as a serious environmental problem, causing a series of damages to the ecosystem, mainly from its complex chemical structures and high stability requiring the use of Advanced Oxidative Processes (AOPs) to promote correct and appropriate treatment [1]. Among POAs, heterogeneous photocatalysis presents the best alternative due to the formation of oxidative species, mainly the hydroxyl radical (•OH), promoting an oxidation-reduction reaction to promote the degradation or mineralization of organic substances into intermediate products or $CO_2$ and $H_2O$. [2]. Furthermore, metallic nanoparticles (MNPs) of $TiO_2NPs$ and ZnONPs have essential properties for the removal of organic pollutants, such as high surface area and porosity. [3]. In this context, the present work aims to synthesize, characterize and evaluate the photocatalytic activity of the $TiO_2NPs@ZnONPs$ for the Rh 6G photodegradation under visible radiation.

## Material and Methods

**1. Synthesis:** $TiO_2NPs$ were synthesized by green synthesis method [4], where 0.25 mL of $C_{12}H_{28}O_4Ti$ (1 mol $L^{-1}$) were mixed with *Aloe vera* extract under magnetic stirring (250 rpm / 90 min), followed of drying of the nanostructured precipitate formed at 333.15 ± 2 K (720 min). For the ZnONPs, 20 mL of the *E. grandis* extract were mixed with 2 g of ZnO (Synth) under magnetic stirring (250 rpm / 353.15 K $min^{-1}$ / 75 min), followed of the calcined (285.15 K $min^{-1}$ / 773.15 ± 2 K / 120 min) [5]. $TiO_2NPs@ZnONPs$ were prepared from mixtures of $TiO_2NPs$ and ZnONPs (ratio 0.6:0.4) under magnetic stirring for (250 rpm / 120 min) and dried at (333.15 ± 2 K / 720 min) by the impregnation method.

**2. Characterization:** The samples were determined by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), $N_2$ porosimetry, Field Emission Gun - Scanning Electron Microscope (FEG-SEM) and zeta potential (ZP).

**3. Photocatalytic Activity:** The Rh 6G dye was used as target pollutant target and $TiO_2NPs@ZnONPs$ as a catalyst, which consisted of two steps: (a) dark stage: equilibrium of the Rh 6G molecules by adsorption/desorption onto the $TiO_2NPs@ZnONPs$ surface for 60 min; and (b) photocatalytic step: aliquots were collected in 0 -180 min, filtered ($\phi$ = 0.45 µm) and diluted (1:10 v $v^{-1}$). The reaction measurement was performed by UV-VIS spectrophotometer analysis at 527 nm.

## Results and Discussion

According to Figure 1(a), $TiO_2NPs@ZnONPs$ showed characteristic peaks of $TiO_2NPs$ of anatase with crystalline planes at 25.09° (101), 47.82° (200) and 54.87° (211), and an average crystallite diameter of 34 nm. The ZnONPs denoted zincite phase at 31.61° (100), 34.22° (002), 36.01° (101), 47.40° (102), 56.31° (110), 62.62° (103), 67.75° (112), and 68.81° (201) and crystallite size of 41 nm confirming the effectiveness of the impregnation. Figure 1(b) presents the FTIR spectrum of $TiO_2NPs@ZnONPs$, where the stretching vibration at 3450 $cm^{-1}$ and 1630 $cm^{-1}$ are related to the stretching vibration of the H-O-H bond and the bending vibration of the H-O bond, respectively. The $TiO_2$NPs@ZnONPs showed the stretching band of the Ti-O-Ti bond at 530 $cm^{-1}$and the band related to the stretching vibrations of the Zn-O around 470 $cm^{-1}$. Figure 1(c) shows the $N_2$ adsorption/desorption isotherm, where $TiO_2$NPs@ZnONPs demonstrated a V-type isotherm and an H1 hysteresis curve with $S_{BET}$ = 63 ± 0.3 $m^2$ $g^{-1}$, Dp = 10.5 ± 0.3 nm, Vp = 0.2 ± 0.03 $cm^3$ $g^{-1}$, ZP = - 14.43 ± 0.2 mV facilitating the process of adsorption of Rh 6G molecules and heterogeneous photocatalysis due to the high surface area (> 50 $m^2$ $g^{-1}$) and pore diameter of 2-50 nm generating hydroxyl radical by redox reactions.

Figure 1(d) shows FEG-SEM micrography of the $TiO_2$NPs@ZnONPs where presented a heterogeneous morphology with porous rod and spherical particles around 112.26 ± 35.2 nm. Figure 1(e) shows the kinetic curve for the Rh 6G photodegradation 32.01% removal after 180 min under visible radiation using the condition of [$TiO_2$NPs@ZnONPs] of 1 g $L^{-1}$, [Rh 6G] of 20 mg $L^{-1}$, pH 7 at T of 298.15 ± 2 K demonstrating an apparent pseudo first order reaction in Figure 1(f) of the $k$ = 0.0027 $min^{-1}$.

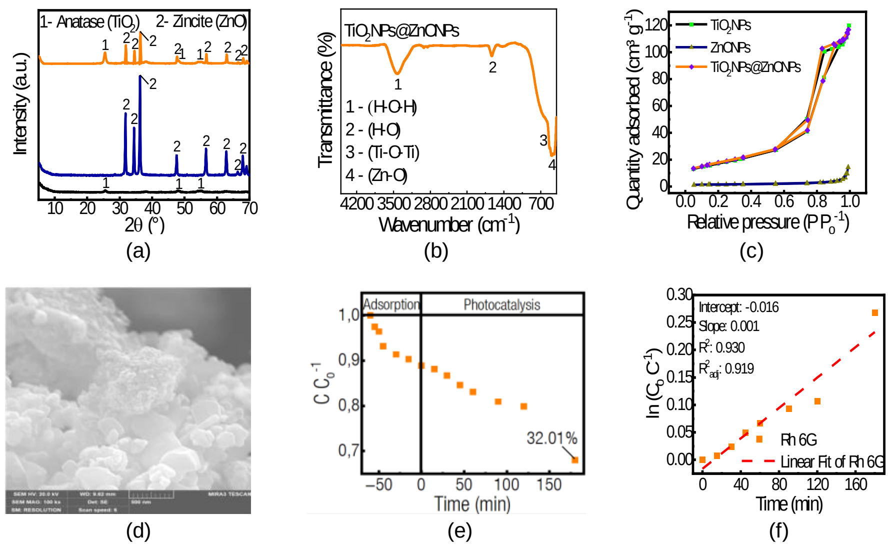



**Figure 1.** (a) X-ray diffractogram; (b) FTIR spectrum; (c) $N_2$ adsorption/desorption isotherms; (d) FEG-SEM micrographs with 100kx; (e) Photocatalytic activity of the $TiO_2$NPs@ZnONPs; and (f) linear transform ln ($C_0$ $C^{-1}$) for the Rh 6G photodegradation under visible radiation.

## Conclusions

$TiO_2$NPs@ZnONPs was synthesized by the green synthesis method from *Aloe Vera* and *E. grandis* extracts for the Rh 6G photodegradation under visible irradiation. The condition was [Rh 6G] = 20 mg $L^{-1}$, [$TiO_2$NPs@ZnONPs] = 1 g $L^{-1}$ and pH = 7 with 32.01 % ($k$ = 0.0027 $min^{-1}$). Therefore, the bimetallic nanocomposite presents photocatalytic activity for application in the removal of wastewater with dyes.

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