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## Solar-active photocatalytic tandems. A compromise in the photocatalytic processes design

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### ABSTRACT

The quest for Vis- or solar-active photocatalytic materials and working systems led to various solutions, aiming at high process efficiency, towards mineralization. This involves the pH-adjustment (supporting the pollutant adsorption on the photocatalyst) and the addition of electron trappers, as H<sub>2</sub>O<sub>2</sub>. While these may be effective on the process efficiency, they also can have photo-corrosion side effects, reducing the up-scaling potential.

The paper presents a three-layered tandem system of SnO<sub>2</sub>/Cu<sub>x</sub>S/TiO<sub>2</sub>, and proves its activity under artificial solar radiation in the phenol photodegradation. The effect of pH (3–9) is comparatively analysed considering the electrostatic interactions substrate – pollutant (based on pzc and pKa), the speciation of the oxidative species (particularly the pH-dependent equilibria) and the photocatalyst stability, evaluated based on changes in surface morphology and optical transmittance. The results show the need to optimize the photocatalytic process design with a compromise between the electrostatic attraction and the photo-corrosion conditions and outlines the neutral pH as best meeting the efficiency and stability prerequisites.

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### 1. Introduction

Advanced oxidation processes based on the generation of highly reactive hydroxyl species able to oxidize/mineralize a broad range of organic pollutant, including dyes, phenols, pesticides, etc., proved to be effective in wastewaters treatment [1–4]. Homogeneous photolysis is already reported at pilot level but has the main drawback of potentially toxic by-products. Therefore, heterogeneous photocatalysis is intensively investigated, particularly aiming at mineralization of organic pollutants, thus contributing to the effort focused on reducing the *water stress* through a wastewater treatment able to deliver the end-product at the quality required for water re-use [5].

The process has significant advantages, including the efficient removal of recalcitrant pollutants at low concentrations and no sludge formation; however, the high costs of the process (UV radiation, photocatalytic materials and efficiency) limits the application at industrial scale, [6]. Up-scaling the technology imposes requirements on the use of sunlight, but also on the photocatalyst stability in the working conditions and its good resistance at photo corrosion (secondary phenomena that can accompany

photocatalysis). Thus, the main prerequisites for up-scaling are as follows: low cost, solar-active photocatalysts with good stability over a broad pH range (or a well-defined working pH), easy recoverable and active for a long operation time [7].

Thousands of papers report on TiO<sub>2</sub> based photocatalysis [1–4]; the main drawbacks refer to the fast charge recombination and the need of UV radiation to activate the process ( $E_g=3.2$  eV [2]). A possible solution to extend its photo activity giving use to the solar radiation, is the development of composite photocatalysts in double/three layered tandem structures, by coupling TiO<sub>2</sub> with other semiconductors with suitable electronic band structure including Cu<sub>x</sub>S, CuInS<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, ZnO [1,2].

Following the concept of the 3rd generations of photovoltaics, the multi-layered structures involving wide and narrow band gap semiconductors (oxides and sulfides) allow reducing the effective band gap and give use to the radiation in different spectral domains, including Vis; the addition of a chemically inert oxide (as TiO<sub>2</sub>) as outer layer will further support the durability of these tandems in the aqueous working conditions. These type of structures have the advantage of a good control of the optoelectronic response, giving the possibility of shifting towards Vis in a larger extent than the currently employed doping strategies.

This paper investigates the photocatalytic activity of a tandem photocatalyst based on SnO<sub>2</sub>–Cu<sub>x</sub>S (Cu<sub>x</sub>O)–TiO<sub>2</sub>, using phenol as reference pollutant, under simulated solar radiation. The influence

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of different experimental parameters (pH, pollutant concentration) on the photodegradation process is investigated and the process design is discussed.

## 2. Experimental

### 2.1. Preparation of the three components composite photocatalytic systems

The multi-component composite systems,  $\text{SnO}_2\text{-Cu}_x\text{S}(\text{Cu}_x\text{O})\text{-TiO}_2$  ( $\text{Sn}_{\text{CuTi}}$ ) was obtained as previously reported [1], by robotic spray pyrolysis deposition of successive thin layers of tin oxide, copper oxide/copper sulfides ( $\text{Cu}_x\text{S}$ ) and titanium dioxide, using microscopic glass as substrate. The individual metal oxide layers were synthesized using metal chlorides as precursors and ethanol as solvent. Copper sulfide results from the reaction of copper chloride and thiourea in a water–alcoholic medium.

### 2.2. Photocatalysis experiments

The photo-degradation experiments were done in a home-made reactor using simulated solar radiation, that combines UV (15%, one black light tube F18 W/T8, UVA, typically 340–400 nm, with  $\lambda_{\text{max}}=365$  nm, flux intensity 3 lx, Philips) and Vis sources (85%, two TL-D Super 80 18 W/865, Vis white cold light tubes, typically 400–700 nm, with  $\lambda_{\text{max}}=565$  nm, flux intensity 28 lx, Philips), placed annular to the photocatalytic system.

The photocatalytic activity of the tandem thin film ( $2 \times 2 \text{ cm}^2$ ) was evaluated in the phenol degradation ( $c=4, 10, 20$  ppm) at different pH values,  $\text{pH}=3\text{--}9$ . The pH was adjusted using HCl or NaOH. Before irradiation, each sample (photocatalyst immersed in 25 mL solution) was kept for 2 h in dark, to reach the adsorption–desorption equilibrium. The pollutant concentration was hourly estimated up to 6 h of photo-degradation, and the process efficiency was calculated, according to Eq. (1)

$$\eta = \frac{c_0 - c}{c_0} 100 \quad (1)$$

where  $c_0$  represents the initial and  $c$  the current phenol concentrations, evaluated based on the on the calibration curve registered on a UV–vis–NIR spectrometer, (Perkin Elmer Lambda 25) at the maximum absorption peak for phenol ( $\lambda=270$  nm).

Each experiment was run in triplicate and the mean value was presented. The deviation among the values was of max 8.3%.

### 2.3. Materials characterization

The degradation of the photocatalyst in the pollutant solution was evaluated by measuring the optical transmittance of the layers before and after 6 h of photocatalysis. The results are expressed as the percentage of transmittance increase. The corresponding changes in the morphology were recorded by surface analysis using scanning electron microscopy (SEM S-3400N-Hitachi).

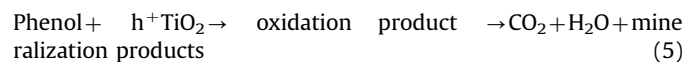
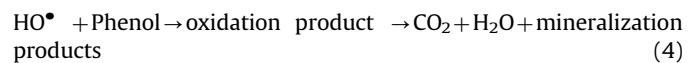
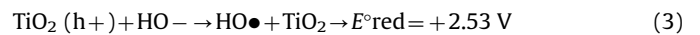
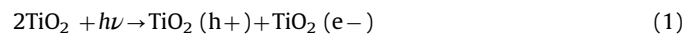
## 3. Results and discussions

The photocatalysis efficiency is significantly influenced by parameters that represent input data in the process design: initial pollutant concentration, working pH, catalyst load, radiation type and intensity, oxygen or oxidants addition, charge carrier trappers or other redox couples, process duration, etc., [8]. Previous research showed that the  $\text{SnO}_2\text{-Cu}_x\text{S}(\text{Cu}_x\text{O})\text{-TiO}_2$  tandem photocatalyst allows methylene blue mineralization up to 75% under solar irradiation in optimized pH conditions [1], as result of

cumulative charge generation followed by the formation of highly oxidative species. The good mobility of the charge carriers through the systems and the reduced recombination were obtained through suitable band gap alignment and by developing uniform and continuous interfaces between the components grown as rather small but compact crystallites ( $\text{TiO}_2$  8.9 nm,  $\text{CuO}/\text{Cu}_x\text{S}$  26.4 nm and  $\text{SnO}_2$  8.7 nm), with an overall crystallinity degree of 96.9%.

This work further extends the investigations aiming at outlining the optimal process design, by using a reference pollutant, phenol, well recognized for its stability.

Electron–hole pairs are formed when the tandem photocatalyst is irradiated with suitable energy, higher than the effective band gap of the semiconductor assembly; the holes can directly oxidize the phenol molecules or can be further involved in the generation of oxidizing species ( $\text{HO}^\bullet$ ) that degrade phenol according to the mechanism described by Eqs. (1)–(5) [3,9]. The first specie involved in the photocatalytic reactions is  $\text{TiO}_2$ , the top layer of the tandem, thus charge generation is primarily here expected



Parallel reductions can develop at the photocatalyst surface, involving the photo generated electrons and  $\text{TiO}_2$  ( $\text{Ti}^{4+}/\text{Ti}^{3+}$ ,  $E^\circ_{\text{red}} = -0.52 \text{ V}$ ) or the oxygen adsorbed onto the surfaces leading to  $\text{O}_2^- \bullet$  or  $\text{HO}^\bullet$  formation.

Three parallel sets of experiments were run to investigate the role of the initial phenol concentration on the photo degradation process (Fig. 1).

Higher efficiencies, thus a faster phenol concentration decay, are recorded for each pH value in the mostly diluted samples (4 ppm phenol, Fig 1c) proving that photocatalysis should be employed, after conventional wastewater treatment processes that reduce, but not completely remove the recalcitrant pollutant.

As the data in Fig. 1 show, adsorption (in dark) is almost insignificant at low phenol concentrations (4 ppm), when diffusion hinders the process. Oppositely, during the experiments that allowed obtaining the highest efficiencies ( $\text{pH}=7$ ), adsorption reached 0.7% for the 20 ppm phenol solution and 0.5% for the 10 ppm one; these values represent 10% and respectively 8.5% from the overall removal efficiencies, thus the effect of the initial concentration could be correlated with the number of pollutant molecules or by-products that compete to adsorb onto the active sites of a given amount of photocatalyst, and the number of photons per surface unit (constant in a given time under constant irradiation intensity). When increasing concentration, the probability of phenol molecules to react with  $\text{HO}^\bullet$ /holes increases, but the number of generated oxidizing species is limited as the photocatalytic surface may be partially clogged, leading to reduction in the degradation rates/efficiencies. These facts are in good agreement with other literature data [2–4].

Additionally, in aqueous solutions, equilibrium reactions described by Eqs. (6)–(9) involve the dissolved oxygen, protons, hydroxyl in the phenol photo-degradation. These reactions are pH dependent, thus any pH variation generates a shift in the equilibrium to balance the excess. Similarly, there is a shift in the values

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