

# 1 Photocatalytic removal of Patent Blue V dye on Au-TiO<sub>2</sub> and Pt-TiO<sub>2</sub> catalysts

2 Vincenzo Vaiano<sup>1\*</sup>, Giuseppina Iervolino<sup>1</sup>, Diana Sannino<sup>1</sup>, Julie J. Murcia<sup>2</sup>, Maria C. Hidalgo<sup>3</sup>,

3 Paolo Ciambelli<sup>1</sup> and José A. Navío<sup>3</sup>

4 *1- Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II, 132, 84084*

5 *Fisciano (SA) Italy*

6 *2- Grupo de Catálisis de la Universidad Pedagógica y Tecnológica de Colombia, Avenida Central*

7 *del Norte, Tunja – Boyacá – Colombia*

8 *3- Instituto de Ciencia de Materiales de Sevilla (ICMS), Consejo Superior de Investigaciones*

9 *Científicas (CSIC), Universidad de Sevilla, Américo Vespucio 49, 41092 Sevilla – Spain.*

10 \* *vvaiano@unisa.it*

## 11 Abstract

12 In this work it was studied the efficiency of a photocatalytic process for the removal of Patent blue  
13 V. This dye is very difficult to remove by conventional treatments such as adsorption or coagulation  
14 therefore the photocatalytic process is a very interesting alternative for the removal this dye mainly  
15 because it does not require expensive oxidants and it can be carried out at mild temperatures and  
16 pressures. In this work it was tested the efficiency of Au-TiO<sub>2</sub> and Pt-TiO<sub>2</sub> photocatalysts in the  
17 Patent blue V removal. The Au-TiO<sub>2</sub> catalysts were prepared by two different methods: chemical  
18 reduction and photochemical deposition; Pt-TiO<sub>2</sub> catalysts were obtained only by photochemical  
19 deposition. In the synthesis of the catalysts prepared by photochemical deposition, it was evaluated  
20 the influence of some parameters, such as deposition time and the intensity of the light source over  
21 the physicochemical properties and photocatalytic activity of the materials obtained. An analysis of  
22 the effect of the catalyst dosage and initial Patent blue V concentration over the dye degradation  
23 efficiency was also attempted.

24 In general, it was observed that the presence of Au or Pt on TiO<sub>2</sub> enhances the Patent blue V  
25 photodegradation; it was found that noble metal particle size and distribution on TiO<sub>2</sub> surface are  
26 important factors influencing the dye removal. The highest dye degradation was obtained over the

1 Au-TiO<sub>2</sub> catalyst prepared by photochemical deposition, using high light intensity and 15 minutes  
2 of deposition time during the synthesis. A discoloration and a total organic carbon (TOC) removal  
3 of 93 and 67% respectively, were obtained over this material after 180 minutes of UV irradiation.  
4 These values are higher than that the obtained on S-TiO<sub>2</sub> (discoloration and TOC removal of about  
5 25% and 3%, respectively).

6  
7 **Keywords:** Photocatalysis, Patent blue V dye, Au-TiO<sub>2</sub>, Pt-TiO<sub>2</sub>, photocatalysts preparation  
8 method.

## 10 1. Introduction

11 A substantial amount of hazardous organic compounds are introduced into the environment as a  
12 result of the industrial activities. Currently, dyestuffs coming from textile and food industries are  
13 important pollutants in water effluents. These dyes represent a serious problem for the human and  
14 animal health. For that reason, the degradation of these pollutants has acquired increasing attention.  
15 Heterogeneous photocatalysis has been studied in the decomposition of a wide range of undesirable  
16 chemical contaminants and it appears to be a feasible process for the degradation of dyes in water  
17 courses by using solar or artificial light illumination [1-4]. TiO<sub>2</sub> is the semiconductor most widely  
18 studied and used in photocatalytic processes. In order to improve the photoactivity of this oxide,  
19 many strategies, such as sulfation and noble metal addition, have been employed [3, 5, 6]. For the  
20 noble metal addition on TiO<sub>2</sub> surface, many methods have been employed, resulting in different  
21 metal particle sizes. The presence of metal nanoparticles decreases the electron-hole recombination,  
22 thus improving the TiO<sub>2</sub> efficiency in the photodegradation reactions. It has been reported that the  
23 improvement of TiO<sub>2</sub> photoactivity by noble metal addition depends not only on metal content but  
24 also on TiO<sub>2</sub> properties, metal particle size and metal oxidation state [7-10]. So it is very important

1 to control the synthesis parameters in order to obtain highly effective photocatalysts based on  
2 modified TiO<sub>2</sub>.

3 Patent blue V (PB) is a recognized dye in food industry. This compound is difficult to remove with  
4 conventional treatments such as adsorption or coagulation. As alternative the photocatalytic  
5 degradation of PB has been investigated and reported in literature by using TiO<sub>2</sub> in presence of  
6 different electron acceptors such as H<sub>2</sub>O<sub>2</sub> or KBrO<sub>3</sub> [11, 12] or using TiO<sub>2</sub>-coated nonwoven fibers  
7 [13]. In the present work it was evaluated the photodegradation of the PB over sulfated and  
8 metallized TiO<sub>2</sub> (Au-TiO<sub>2</sub> and Pt-TiO<sub>2</sub>). It was also evaluated the effect of the Au or Pt addition and  
9 the synthesis parameters over the efficiency of these materials in the PB removal. At our  
10 knowledge, it is the first paper reporting the use of TiO<sub>2</sub> metallized with noble metals in a  
11 photocatalytic system for the removal of PB dye.

## 12 **2. Experimental**

### 13 **2.1 Synthesis of the photocatalysts**

#### 14 **2.1.1 Sulfated TiO<sub>2</sub>**

15 TiO<sub>2</sub> used as starting material was prepared by the hydrolysis of titanium tetraisopropoxide  
16 (Aldrich, 97%) in isopropanol solution (1.6 M) by the slow addition of distilled water (volume ratio  
17 isopropanol/water 1:1). Afterward, the generated precipitate was filtered, dried at 110°C overnight  
18 and calcined at 650 °C for 2 hours. Sulfation treatment was applied to TiO<sub>2</sub> before calcination; the  
19 TiO<sub>2</sub> powders were sulfated by immersion in H<sub>2</sub>SO<sub>4</sub> aqueous solution 1 M for 1 hour and afterward  
20 calcinated at 650 °C for 2 hours (S-TiO<sub>2</sub>). Sulfation treatment was carried out for two reasons; on  
21 one hand, previous results have shown that sulfation stabilizes the anatase phase up to high  
22 temperatures and protect the catalyst from the loss of surface area by sintering [14]. On the other  
23 hand, at the calcination temperature of 650 °C, the elimination of sulfate groups promotes the  
24 creation of high number of oxygen vacancies, which have been reported as preferential sites for  
25 noble metal adsorption [15].

1 The S-TiO<sub>2</sub> powders were also modified by noble metal addition. Two different methods were  
2 employed: the photochemical deposition and chemical reduction method. The typical procedure is  
3 described as follows.

#### 4 ***2.1.2 Photochemical deposition (PD) of gold and platinum over S-TiO<sub>2</sub>***

5 Gold (III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O, Aldrich 99.9%) or Hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>,  
6 Aldrich 99.9%) were used as metal precursors for Au and Pt, respectively. Under an inert  
7 atmosphere (N<sub>2</sub>), a suspension of S-TiO<sub>2</sub> in distilled water containing isopropanol (Merck 99.8%)  
8 which acts as sacrificial donor, was prepared. Then, the appropriate amount of metal precursor to  
9 obtain a nominal Pt or Au loading of 0.5 weight total (wt %) to TiO<sub>2</sub> was added. Final pH of the  
10 suspensions was 3. Photochemical deposition of Pt or Au was then performed by illuminating the  
11 suspensions with an Osram Ultra-Vitalux lamp (300W) with a sun-like radiation spectrum and a  
12 main emission line in the UVA range at 365 nm, using 15 and 120 minutes of photodeposition time.  
13 Light intensities on the TiO<sub>2</sub> surface were low intensity 0.15 W/m<sup>2</sup> (LI) and high intensity 140  
14 W/m<sup>2</sup> (HI) for Pt and Au photochemical deposition, respectively.

15 After noble metal deposition, the powders were recovered by filtration and dried at 110 °C  
16 overnight. The metallized samples were called Au-TiO<sub>2</sub> and Pt-TiO<sub>2</sub>.

#### 17 ***2.1.3 Chemical reduction (CR) of gold over S-TiO<sub>2</sub>***

18 Chemical reduction of gold was carried out by using sodium citrate as both reducing and stabilizing  
19 agent following a procedure described in the literature [16]. Appropriate amount of HAuCl<sub>4</sub> for  
20 nominal content of deposited Au of 0.5 wt. % with respect to TiO<sub>2</sub> was dissolved in distilled water  
21 (1 mg HAuCl<sub>4</sub>/10 mL water). Then, suspensions of the different TiO<sub>2</sub> samples (1 g) in sodium  
22 citrate solutions (0.2 g/10 mL distilled water) were added. The final suspensions were heated to  
23 reflux for 1 h under N<sub>2</sub> atmosphere to avoid gold re-oxidation. After this time, the powders were  
24 washed, filtered and dried at 110 °C overnight.

25 All the photocatalysts synthesized are enlisted in Table 1.

## 26 **2.2 Characterization of the photocatalysts**

1 All the materials were widely characterized using different techniques. Specific surface area ( $S_{\text{BET}}$ )  
2 measurements were carried out using low-temperature  $\text{N}_2$  adsorption in a Micromeritics ASAP  
3 2010 instrument. Degasification of the samples was performed at  $150^\circ\text{C}$ .

4 Gold and platinum particles morphology was evaluated by Scanning electron microscopy (SEM),  
5 Field Emission SEM images were obtained in a Hitachi S-4800 microscope. Transmission Electron  
6 Microscopy (TEM) was performed in a Philips CM200 instrument. In both techniques, samples  
7 were dispersed in ethanol using an ultrasonicator and dropped on a carbon grid.

8 Determination of the metal particle average diameter ( $\bar{d}$ ) in the different samples was accomplished  
9 by counting particles in a high number of TEM images from different places of the samples. The  
10 following equation was used:  $(\bar{d}_{\text{nm}}) = \sum di \times fi$

11 Where  $di$  is the diameter of the  $ni$  counted particles and  $fi$  is the particle size distribution estimated  
12 by:

$$fi = \frac{ni}{\sum ni}$$

14 Where  $ni$  is the number of particles of diameter  $di$ .

15 Crystalline phase composition and degree of crystallinity of the samples were estimated by X-ray  
16 diffraction (XRD). XRD patterns were obtained on a Siemens D-501 diffractometer with Ni filter  
17 and graphite monochromator using  $\text{Cu K}\alpha$  radiation. Anatase crystallite sizes were calculated from  
18 the line broadening of the main anatase X-ray diffraction peak (1 0 1) by using the Scherrer  
19 equation. Peaks were fitted by using a Voigt function.

20 Light absorption properties of the samples were studied by UV–Vis spectrophotometry. The UV–  
21 Vis DR spectra were recorded on a Varian spectrophotometer model Cary 100 equipped with an  
22 integrating sphere and using  $\text{BaSO}_4$  as reference. Band-gaps values were calculated from the  
23 corresponding Kubelka–Munk functions,  $F(R_\infty)$ , which are proportional to the absorption of  
24 radiation by plotting  $(F(R_\infty) \times h\nu)^{1/2}$  against  $h\nu$  [6]. Chemical composition and total noble metals

1 content in the samples were determined by X-ray fluorescence spectrometry (XRF) in a Panalytical  
2 Axios sequential spectrophotometer equipped with a rhodium tube as the source of radiation. XRF  
3 measurements were performed onto pressed pellets (sample included in 10 wt.% of wax).

4 X-ray photoelectron spectroscopy (XPS) studies were carried out on a Leybold–Heraeus LHS-10  
5 spectrometer, working with constant pass energy of 50 eV. The spectrometer main chamber,  
6 working at a pressure  $<2 \times 10^{-9}$  Torr, is equipped with an EA-200MCD hemispherical electron  
7 analyzer with a dual X-ray source working with Al  $K\alpha$  ( $h\nu = 1486.6$  eV) at 120 W and 30 mA. C 1s  
8 signal (284.6 eV) was used as internal energy reference in all the experiments. Samples were  
9 outgassed in the prechamber of the instrument at  $150^\circ\text{C}$  up to a pressure  $< 2 \times 10^{-8}$  Torr to remove  
10 chemisorbed water.

11

### 12 **2.3 Photocatalytic experiments**

13 Photocatalytic experiments were carried out with a Pyrex cylindrical reactor (ID = 2.5 cm) equipped  
14 with an air distributor device. The photoreactor was irradiated by a strip composed of 15 UV-LEDs  
15 (nominal power: 10W) with wavelength emission in the range 375–380 nm. The LEDs strip was  
16 positioned around the external surface of the reactor so that the light source uniformly irradiated the  
17 reaction volume (light intensity:  $570 \text{ W/m}^2$ ). The catalyst dosage was 3 g/L in an 80 ml aqueous  
18 solution containing 7 mg/L of PB. Continuous mixing of the solution in the reactor was assured by  
19 external recirculation of water through a peristaltic pump; the suspension was left in dark conditions  
20 for 120 minutes to reach the adsorption-desorption equilibrium of PB on the photocatalysts surface,  
21 and then the photocatalytic reaction was initiated under UV light for up to 180 minutes.

22 In order to compare the effect of the dye concentration and the photocatalyst dosage, different  
23 values of these parameters were evaluated. Thus, the initial concentrations of patent blue were 3, 7  
24 and 12 mg/L; the catalysts dosages were 3, 6, 9 and 12 g/L.

## 2.4 Analytical measurements

The color of aqueous samples was determined with a Perkin Elmer UV-Vis spectrophotometer at  $\lambda_{\text{max}} = 635$  nm. The TOC was measured by the high temperature combustion method on a catalyst (Pt-Al<sub>2</sub>O<sub>3</sub>) in a tubular flow microreactor operated at 680 °C, with a stream of hydrocarbon free air to oxidize the organic carbon. Laboratory apparatus consisted of mass flow controllers (Brooks) operating on each gas; an injection system; a NDIR continuous analyzer (Hartmann & Braun Uras 10E) for measurements of CO and CO<sub>2</sub> concentrations at the combustion reactor outlet and a paramagnetic analyzer (Hartmann & Braun Magnos 6G) for continuous monitoring of O<sub>2</sub>.

## 3. Results and discussion

### 3.1 Characterization of the photocatalysts

In order to correlate the physicochemical properties of the catalysts with their photocatalytic activity, all the materials were widely characterized by using different techniques and the results obtained are summarized in Table 1 and presented below.

#### 3.1.1 N<sub>2</sub> physisorption

The specific surface areas ( $S_{\text{BET}}$ ) of the photocatalysts analyzed are listed in Table 1. As it can be observed, the BET surface area of S-TiO<sub>2</sub> is 58 m<sup>2</sup>/g. After the metal addition a slight decrease of the  $S_{\text{BET}}$  value was detected, probably due to pore blocking by metal nanoparticles homogeneously distributed on surface. As it can be seen in Table 1, this effect is much more noticeable in the catalysts prepared by chemical reduction and also in the materials prepared by photochemical deposition method using 15 minutes of deposition time.

#### 3.1.2 Microscopic analysis

In order to obtain information about the metal deposits size and dispersion, all the samples modified by gold or platinum addition were studied by SEM. Figure 1 shows representative SEM images of the metallized samples prepared by chemical reduction (CR) and photochemical deposition method

1 (PD), using  $140 \text{ W/m}^2$  of light intensity (HI) and different deposition times (15 and 120 min).  
2 Images of the samples prepared using low intensity ( $\text{LI} = 0.15 \text{ W/m}^2$ ) are not provided for the sake  
3 of brevity. In all the samples, gold or platinum particles can be seen as white spots placed over the  
4 larger  $\text{TiO}_2$  particles. As it can be observed, there are significant differences in particles sizes and  
5 morphology between samples prepared by PD or by CR. Thus, in the catalyst Au- $\text{TiO}_2$  prepared by  
6 CR (Figure 1C), the gold particles are more homogeneously distributed on  $\text{TiO}_2$  surface than the  
7 gold particles observed in the samples prepared by PD (Figure 1A and B). The higher number of  
8 gold particles covering the  $\text{TiO}_2$  surface can explain the lowest  $S_{\text{BET}}$  value observed in the sample  
9 prepared by CR (Table 1).

10 It was also possible to observe that the platinum particles are smaller than the gold particles in the  
11 metallized samples prepared by PD, and in all the cases the number and size of the metal particles  
12 increase with the deposition time from 15 to 120 min. The average particle size of the noble metal  
13 (Au or Pt) particles, obtained by TEM analysis is presented in Table 1; selected TEM images of the  
14 samples metallized prepared by photochemical deposition method, using the highest light intensity  
15 and different deposition times are presented in Figure 2. In these images it is possible to observe  
16 that gold particles with higher sizes are heterogeneously distributed and partially covering the  $\text{TiO}_2$   
17 surface; the number and the size of the gold particles increases with the deposition time. On the  
18 contrary, in the case of the Pt- $\text{TiO}_2$  sample, platinum particles with the lowest sizes are  
19 homogeneously covering the titania surface.

20

### 21 *3.1.3. X-ray diffraction (XRD)*

22 XRD was used to analyze the effect of the metal addition on the crystallite structure and phase  
23 composition of sulfated  $\text{TiO}_2$ . Figure 3 shows the XRD patterns of the sulfated  $\text{TiO}_2$  and the  
24 metallized catalysts prepared by CR and PD using high light intensity and 120 min of deposition  
25 time.



1 In all the analyzed samples, only anatase peaks ( $25.3^\circ$ ,  $38.0^\circ$ ,  $48.0^\circ$  and  $54.7^\circ$   $2\theta$ ) were detected.  
2 The stabilization of anatase phase of the  $\text{TiO}_2$  by the sulfation pretreatment can be noticed here, as  
3 no traces of rutile were found even after the high calcination temperature used during the  
4 preparation of the catalysts [14].  
5 The anatase crystallite size in the different samples was determined from the broadening of  
6 corresponding X-ray diffraction peaks by using Scherrer equation and these data are listed in Table  
7 1. As it can be observed, for sulfated samples the anatase crystallite size was about 20 nm, any  
8 important influence of the synthesis parameters over this value was observed. No peaks ascribed to  
9 platinum or gold species were detected in the XRD patterns of the metallized samples; surely due to  
10 the low metal content in the samples or due to the detection limit of this technique.  
11 XRD patterns of the catalysts prepared by PD under low light intensity are not included for the sake  
12 of brevity, but the diffraction peaks are similar than the observed for the samples obtained at high  
13 light intensity.

14

#### 15 *3.1.4 UV-Vis diffuse reflectance spectra (UV-Vis DR)*

16 The UV-Vis DR spectra of selected samples are shown in Figure 4. The typical band edge of the  
17  $\text{TiO}_2$  semiconductor was observed at around of 370 nm for all the samples. Gold or platinum  
18 addition did not alter substantially the absorption properties of the samples; however, a slight  
19 increase of absorbance throughout the visible range of the spectrum was observed due to the purple  
20 or grey color of the metallized materials, respectively. In the Au- $\text{TiO}_2$  catalysts, the surface plasmon  
21 resonance band of metallic gold can be observed; this characteristic plasmon is located around 550  
22 nm. It is known that for colloidal gold nanoparticles there is a strong dependence between particle  
23 size and plasmon bandwidth and position [17-19].

24 From the UV-Vis DR spectra, band gaps energies were calculated and the obtained results are  
25 reported in Table 1, being 3.20 eV for the S- $\text{TiO}_2$  sample. Any important modification of this value

1 was observed after gold addition. A slight decrease of the band gap value was observed in the Pt-  
2 TiO<sub>2</sub> samples.

### 3 *3.1.5. X-ray fluorescence*

4 The real gold and platinum content in the metallized samples was measured by XRF and the results  
5 are enlisted in Table 1. As it can be seen, these values are under the nominal metal content used to  
6 prepare these materials (0.5 wt.%), thus indicating an incomplete reduction of the metal precursor  
7 on TiO<sub>2</sub> surface during the synthesis process. However, it was observed that the amount of  
8 deposited gold or platinum increases with the deposition time and with the light intensity in the  
9 materials prepared by PD method.

10 XRF analysis revealed that a certain amount of S and Cl<sup>-</sup> species remained on the solids after  
11 preparation. The sulfur content in the samples was under 0.16 wt %; the Cl<sup>-</sup> content in all the  
12 platinized samples was under 0.10 wt %; this content comes from the gold and platinum precursors.

### 13 *3.1.6 X-ray photoelectron spectroscopy (XPS)*

14 XPS analyzes were also carried out and the binding energies (BE) of the main XPS peaks (Ti 2p<sub>3/2</sub>  
15 and O 1s) for the different samples are enlisted in Table 1. The Ti 2p<sub>3/2</sub> core level spectra were  
16 similar for all the analyzed samples with peaks centered at 458.4±0.1 eV, corresponding to Ti<sup>4+</sup> in  
17 the TiO<sub>2</sub> network as the main component. In the O 1s region, a peak located at a binding energy of  
18 529.8±0.2 eV was registered in all the samples. This peak is assigned to lattice oxygen in TiO<sub>2</sub>, with  
19 a broad shoulder at higher binding energies ascribed to oxygen in surface hydroxyl groups.

20 From the XPS data, O/Ti ratios were also calculated and it was found that for S-TiO<sub>2</sub> sample the  
21 O/Ti value was 1.70 indicating the presence of a certain amount oxygen vacancies on the surface of  
22 this oxide, in agreement with previous reported results [14] that showed the development of oxygen  
23 vacancies on TiO<sub>2</sub> surfaces due to the sulfation process. The ratios O/Ti for the metallized samples  
24 were higher than the observed in the S-TiO<sub>2</sub> sample, suggesting that the oxygen vacancies are  
25 partially annihilated during the Pt or Au photochemical deposition over the sulfated oxide. The  
26 atomic percentage of metal was calculated by XPS and it was found to be < 0.2% in all the

1 catalysts; in correlation with the XRF results, the metal atomic content increases with the deposition  
2 time and also with the light intensity used in the catalysts preparation.

3

## 4 **3.2 Photocatalytic activity results**

### 5 *3.2.1 Patent blue V photodegradation on Au-TiO<sub>2</sub>*

6 The efficiency of the photocatalysts prepared and characterized was evaluated in the PB removal. In  
7 order to verify that the target dye was converted in a heterogeneous photocatalytic process, blank  
8 experiments were performed. In particular, tests carried out in dark conditions did not evidence any  
9 oxidation activity. Moreover, additional control tests were carried out in the presence of PB dye and  
10 irradiating the photoreactor with UV-LEDs (photolysis reaction) and in the absence of  
11 photocatalyst. Also in this case, no degradation of the target dye was detected.

12 Figure 5 shows the evolution of the discoloration of the PB as a function of run time, obtained over  
13 Au-TiO<sub>2</sub> photocatalysts in comparison with S-TiO<sub>2</sub>. In dark conditions a decrease of PB  
14 concentration was observed during the first 30 minutes of the test and it was almost unchanged up  
15 to 120 minutes, indicating that the adsorption equilibrium of dye on catalyst surface was reached.  
16 After the dark period, the solution was irradiated with UV light and the reaction started to occur. As  
17 it can be observed, an important decrease of the dye concentration was obtained in presence of Au  
18 on titania surface. The highest discoloration was observed on the catalyst Au-TiO<sub>2</sub> prepared by  
19 photochemical deposition method, using high light intensity (140 W/m<sup>2</sup>) and 15 minutes of  
20 deposition time.

21 The evaluation of the TOC during the run time was also analyzed and the obtained results are  
22 represented in Figure 6. In this case it was also observed that the highest mineralization of the dye  
23 was achieved on the sample Au-TiO<sub>2</sub>(PD-HI)15 min. In particular, with this catalyst, a discoloration  
24 and a TOC removal (evaluated starting from the irradiation time) of 93 and 67% respectively, were  
25 obtained after 180 minutes of UV irradiation. These values are higher than that obtained on S-TiO<sub>2</sub>  
26 (discoloration and TOC removal of about 25% and 3%, respectively).

1 The percentage of discoloration and mineralization of the PB evaluated starting from the irradiation  
2 time is summarized in Table 2.

3 In the case of the Au-TiO<sub>2</sub> samples prepared with the highest deposition time (120 min), the  
4 decrease of the photocatalytic activity could be due to the big cluster of gold particles which can act  
5 as a recombination centers, thus reducing the effectiveness of these samples [20]. The best  
6 photocatalytic behavior was observed over the catalyst Au-TiO<sub>2</sub> prepared by photochemical  
7 deposition method, using high light intensity (140 W/m<sup>2</sup>) and 15 minutes of deposition time. It  
8 could be due to a combined effect between two factors: (i) the presence of the gold nanoparticles,  
9 which act as a sink for the electrons, retarding the electron-hole recombination, thus leading to an  
10 improvement of the TiO<sub>2</sub> photoefficiency; (ii) in this catalyst, the gold nanoparticles are  
11 heterogeneously distributed on TiO<sub>2</sub> surface. The lower number of the gold particles allows to the  
12 dye molecule to be adsorbed with the TiO<sub>2</sub> surface. In this case the azo or sulfate groups in the  
13 molecule of dye can act as electron donor [20], leading to a better interaction between substrate and  
14 catalyst surface, thus increasing the dye discoloration efficiency.

15 In the case of the catalysts with the lowest metal particle sizes, such as Au-TiO<sub>2</sub> prepared by  
16 chemical reduction or Pt-TiO<sub>2</sub> catalysts, many particles with low metal particle sizes could covering  
17 the TiO<sub>2</sub> surface, thus leading to difficult adsorption of the dye.

18 Finally, it is important to note that the lowest PB discoloration was obtained over the catalyst Au-  
19 TiO<sub>2</sub> prepared by CR. The discoloration obtained over this catalyst is even lower than the obtained  
20 with the starting S-TiO<sub>2</sub>. This behavior could be related with the presence of remaining material on  
21 catalyst surface coming from the preparation procedure, mainly due to the sodium citrate used as  
22 reducing agent. Thus the remaining material on surface could have a detrimental effect over  
23 effectiveness of the Au-TiO<sub>2</sub>(CR) catalyst on the dye photodegradation. These results can suggest  
24 that photodeposition is a suitable method to prepare active and efficient catalysts for PB  
25 photocatalytic removal.

26

### 3.2.2 Patent blue V photodegradation on Au-TiO<sub>2</sub> – Effect of the initial dye concentration

Taking into account that the best photocatalytic behavior in the PB removal was obtained on Au-TiO<sub>2</sub>(PD-HI)15min catalyst, the effectiveness of this catalyst in the degradation of different initial concentrations (3, 7 and 12 mg/L) of the dye was evaluated.

Figure 7, shows the dye discoloration on the Au-TiO<sub>2</sub>(PD-HI)15 min catalyst. After 120 minutes of dark adsorption, the photocatalytic test started. After 180 minutes of irradiation, the final value of the discoloration was 100% in the case of 3 mg/L, 92% in the case of 7 mg/L and 20% in the case of 12 mg/L PB initial concentration.

For the interpretation of the effect of the dye initial concentration on the photodegradation performances, the Langmuir-Hinshelwood model has been used [21].

Considering that the adsorption equilibrium was reached after 120 min of run time, the behaviour of the amount of PB adsorbed on catalyst as a function of the dye initial concentration ( $C_0$ ) is similar to a Langmuir adsorption isotherm (Figure 8 insert). Thus for the evaluation of PB adsorption on the active surface, the following equation was used:

$$C^* = \frac{b \cdot C_0^*}{1 + b \cdot C_0^*} \quad \text{Eq. (1)}$$

Where  $C^*$  is the amount of PB adsorbed on catalyst ( $g_{\text{dye}}/g_{\text{cat}}$ );  $C_0^*$  is the concentration of PB in solution after dark adsorption (mg/L);  $b$  is the adsorption constant (L/mg).

The Langmuir isotherm can be rearranged to give:

$$\frac{C_0^*}{C^*} = \frac{1}{b \cdot C_m} + \frac{1}{C_m} C_0^* \quad \text{Eq. (2)}$$

Accordingly, a plot of  $C_0^*/C^*$  as a function of  $C_0^*$  produces a straight line with slope =  $1/C_m$  and intercept =  $1/bC_m$  (Figure 8).  $C_m$  is the maximum absorbable value of  $C^*$ .

The value of  $b$  was calculated from Eq. (2) utilizing the data reported in Figure 8 and it was equal to 0.32 (L/mg).

1 With this value it was evaluated the apparent kinetic constant for all the initial concentration of dye,  
2 using the following equation:

$$3 \frac{dC(t)}{dt} = -K \cdot \frac{b \cdot C(t)}{1 + b \cdot C(t)} \cdot a \quad \text{Eq. (3)}$$

4 Where C(t) is the PB concentration (mg/L) as a function of irradiation time; *a* is the e catalyst  
5 dosage (g<sub>cat</sub>/L) and K is the kinetic constant (mg/(g min)).

6 The initial condition of Eq.(3) is:

$$7 \quad t = 0 \quad C(t) = C_0^*$$

8 Eq. (3) together with the initial condition was solved with Euler iterative method to identify the  
9 constants K by fitting the experimental data as a function of irradiation time for the initial dye  
10 concentration of 7 mg/L. The fitting procedure was realized by using the least squares approach  
11 obtaining the value of K: 0.02 [mg/(g min)]. After obtaining the value of K, the experimental data  
12 obtained with different initial dye concentrations were fitted to analyze the ability of the model to  
13 predict the experimental data at 3 and 12 mg/L initial PB concentration. The obtained results are  
14 shown in Figure 9.

15 The calculated values are in good agreement with all the experimental data. It is important to note  
16 that also for the higher initial dye concentration (12 mg/L), this system is able to predict the  
17 discoloration trend with a single value of kinetic constant. Thus the photocatalytic activity is not  
18 dependent by the increase of the intensity of the color meaning that the path length of photons  
19 inside the solution didn't decrease allowing to obtain in an effective way also the mineralization of  
20 the dye (Figure 8).

21

### 22 *3.2.3 Patent blue V photodegradation on Au-TiO<sub>2</sub> – Effect of the catalyst dosage*

23 The effect of the catalyst dosage over the effectiveness of the sample Au-TiO<sub>2</sub>(PD-HI)15min was  
24 evaluated in the range 3-12 g/L and the results of discoloration and TOC removal are presented in  
25 Figures 11 and 12, respectively. After these experiments, it is possible to confirm that the best

1 dosage of catalyst is 9 g/L, obtaining the highest discoloration and mineralization of PB.  
2 Photocatalytic efficiency increased as catalyst loading was increased up to 9 g/L. When the load of  
3 catalyst was increased from 9 to 12 g/L, the discoloration and the mineralization of the dye  
4 decreased. Possibly, the increase in the catalyst dosage over the optimum value resulted in a  
5 decreased light penetration through the solution because of the increased opacity of the aqueous  
6 suspension [22].

#### 7 *3.2.4 Patent blue V photodegradation on Pt-TiO<sub>2</sub>*

8 The effectiveness of the platinized samples in the dye photodegradation was also evaluated. Figure  
9 13 shows the evolution of the discoloration of the PB as a function of run time, obtained over Pt-  
10 TiO<sub>2</sub> photocatalysts in comparison with S-TiO<sub>2</sub>. Also with these catalysts, in dark conditions a  
11 decrease of PB concentration was observed during the first 30 minutes of the test and it was almost  
12 unchanged up to 120 minutes. After the dark period, the solution was irradiated with UV light.  
13 During the irradiation time, it can be observed an increase of the dye degradation. The best  
14 discoloration (85%) and dye mineralization (44%) (Figure 14) was obtained over the catalyst Pt-  
15 TiO<sub>2</sub> prepared by photochemical deposition method and using 120 minutes of deposition time in the  
16 synthesis. These results may be due to the higher Pt content of the photocatalyst prepared with the  
17 highest deposition time.

18

#### 19 *3.2.5 Patent blue V photodegradation - Effect of the kind of noble metal (Au or Pt)*

20 A comparison between the results obtained on the best Au-TiO<sub>2</sub> and Pt-TiO<sub>2</sub> photocatalysts is  
21 shown in Figure 15. As it can be observed, the best performances are obtained with the Au-TiO<sub>2</sub>  
22 catalyst since the TOC removal and discoloration rate under UV irradiation are higher than that  
23 obtained for Pt-TiO<sub>2</sub> catalyst.

24 From the results reported in Table 1, it is possible to note that the catalyst Pt-TiO<sub>2</sub>(PD-HI)120min  
25 has Pt particle size comprised in the range 4-6 nm, while the catalyst Au-TiO<sub>2</sub>(PD-HI)15min has Au  
26 particle size in the range of 30-40 nm, so one would expect that the catalyst Pt-TiO<sub>2</sub>(PD-HI)120

1 min presents a better photocatalytic activity. From the experimental results, instead, it is noted that  
2 the best photocatalytic efficiency is obtained with the catalyst in the presence of Au. In fact, the  
3 literature results reports that Au-TiO<sub>2</sub> shows higher catalytic activity than Pt [23]. Considering that  
4 the noble metals act as a mediator in the vectorial electron-transfer process, their Fermi energy  
5 levels are supposed to affect the interfacial charge transfer and thus the charge separation [24]. In  
6 general, the higher Fermi level of the noble metal leads to the better the photocatalytic activity [25].  
7 In this context, it was found that, for Fermi level, the order of noble metals is of Au > Pt [26],  
8 explaining in this way, the better photocatalytic activity of Au-TiO<sub>2</sub> with respect to Pt-TiO<sub>2</sub> catalyst.

### 3.2.6 *Recyclability of Au-TiO<sub>2</sub> photocatalyst*

11 Recyclability is one of the most important factors in catalysis research [27, 28]. To confirm the  
12 recyclability of Au-TiO<sub>2</sub>(PD-HI)15min sample, the photocatalytic degradation of PB was repeated  
13 up to four cycles (Figure 16). The reduction of discoloration and mineralization percentage was as  
14 low as 1-2% in 60 min of irradiation time. So, these results evidenced the stability of the  
15 photocatalyst and the reproducibility of the process in the PB degradation.

## 4. **Conclusions**

18 In this work the photocatalytic removal of the PB dye with noble metals based photocatalysts has  
19 been addressed for the first time. In particular, it was tested the efficiency of photocatalysts based  
20 on gold or platinum deposited on the surface of sulfated titania, prepared by two different methods:  
21 chemical reduction (CR) and photochemical deposition (PD).

22 It was observed that the presence of Au or Pt on TiO<sub>2</sub> enhances the PB photodegradation and it was  
23 also found that metal distribution on TiO<sub>2</sub> and noble metal particle size are important factors  
24 influencing the dye degradation. There are significant differences in particles sizes and morphology  
25 between samples prepared by PD or by CR. In fact, for the Au-TiO<sub>2</sub> catalyst prepared by CR, the  
26 gold particles are more homogeneously distributed on TiO<sub>2</sub> surface than that observed in the



1 samples prepared by PD. This causes a reduction in the value of the specific surface area for the  
2 sample prepared by CR.

3 The highest dye degradation was obtained over the Au-TiO<sub>2</sub> catalyst prepared by PD method, using  
4 high light intensity and 15 minutes of deposition time during the synthesis.

5 In this catalyst, the Au nanoparticles are heterogeneously distributed and present in lower number  
6 on TiO<sub>2</sub> surface, allows to the dye molecule to have a best contact with the TiO<sub>2</sub> surface.

7 For Pt-TiO<sub>2</sub> catalysts the best discoloration and dye mineralization were obtained over the catalyst  
8 prepared by photochemical deposition method and using 120 minutes of deposition time in the  
9 synthesis. These results may be due to the higher Pt content of the photocatalyst prepared with the  
10 highest deposition time. Comparing the performance of the different catalysts, it can be concluded  
11 that the presence of the noble metal on the TiO<sub>2</sub> surface enhances the removal efficiency of the dye  
12 and that in particular the catalyst with gold showed a better efficiency of removal of PB.

13

#### 14 **Acknowledgements**

15 CITIUS (University of Seville) is acknowledged for XPS and XRF measurements. The authors  
16 wish to thank University of Salerno for funding the project "Sistemi catalitici per l'intensificazione  
17 di processo e per la riduzione dell'inquinamento ambientale" (Ex 60%, anno 2014).

18

#### 19 **References**

- 20 [1] A. Duta, M. Visa, *Journal of Photochemistry and Photobiology A: Chemistry* 306 (2015) 21-  
21 30.  
22 [2] E. Kordouli, K. Bourikas, A. Lycourghiotis, C. Kordulis, *Catal. Today* 252 (2015) 128-135.  
23 [3] J.J. Murcia, M.C. Hidalgo, J.A. Navio, J. Arana, J.M. Dona-Rodriguez, *Appl. Catal., B* 150-  
24 151 (2014) 107-115.  
25 [4] V. Vaiano, O. Sacco, G. Iervolino, D. Sannino, P. Ciambelli, R. Liguori, E. Bezzeccheri, A.  
26 Rubino, *Appl. Catal., B* 176-177 (2015) 594-600.  
27 [5] D. Sannino, V. Vaiano, P. Ciambelli, M.C. Hidalgo, J.J. Murcia, J.A. Navío, *Journal of*  
28 *Advanced Oxidation Technologies* 15 (2012) 284-293.  
29 [6] J.J. Murcia, M.C. Hidalgo, J.A. Navío, V. Vaiano, D. Sannino, P. Ciambelli, *Catalysis*  
30 *Today* 209 (2013) 164-169.  
31 [7] A.V. Vorontsov, I.V. Stoyanova, D.V. Kozlov, V.I. Simagina, E.N. Savinov, *Journal of*  
32 *Catalysis* 189 (2000) 360-369.

- 1 [8] W.Y. Teoh, L. Mädler, R. Amal, *Journal of Catalysis* 251 (2007) 271-280.
- 2 [9] F. Denny, J. Scott, K. Chiang, W.Y. Teoh, R. Amal, *Journal of Molecular Catalysis A:*  
3 *Chemical* 263 (2007) 93-102.
- 4 [10] C. Hu, Y. Tang, J. Zheng, Z. Hao, H. Tang, P.K. Wong, *Appl. Catal., A* 253 (2003) 389-  
5 396.
- 6 [11] M. Saquib, M. Abu Tariq, M. Faisal, M. Muneer, *Desalination* 219 (2008) 301-311.
- 7 [12] R.R. Dalbhanjan, N.S. Pande, B.S. Banerjee, S.P. Hinge, A.V. Mohod, P.R. Gogate,  
8 *Desalination and Water Treatment* (2015).
- 9 [13] C. Fernandez, M.S. Larrechi, M.P. Callao, *Talanta* 79 (2009) 1292-1297.
- 10 [14] G. Colon, M.C. Hidalgo, J.A. Navio, *Appl. Catal., B* 45 (2003) 39-50.
- 11 [15] K. Okazaki, Y. Morikawa, S. Tanaka, K. Tanaka, M. Kohyama, *Phys. Rev. B: Condens.*  
12 *Matter Mater. Phys.* 69 (2004) 235404/235401-235404/235408.
- 13 [16] J. Kimling, M. Maier, B. Okenve, V. Kotaidis, H. Ballot, A. Plech, *J. Phys. Chem. B* 110  
14 (2006) 15700-15707.
- 15 [17] B.K. Min, J.E. Heo, N.K. Youn, O.S. Joo, H. Lee, J.H. Kim, H.S. Kim, *Catal. Commun.* 10  
16 (2009) 712-715.
- 17 [18] S. Link, M.A. El-Sayed, *J. Phys. Chem. B* 103 (1999) 4212-4217.
- 18 [19] M.C. Hidalgo, M. Maicu, J.A. Navio, G. Colon, *J. Phys. Chem. C* 113 (2009) 12840-12847.
- 19 [20] J.J. Murcia, M.C. Hidalgo, J.A. Navio, J. Arana, J.M. Dona-Rodriguez, *Appl. Catal., B* 179  
20 (2015) 305-312.
- 21 [21] D. Sannino, V. Vaiano, O. Sacco, P. Ciambelli, *J. Environ. Chem. Eng.* 1 (2013) 56-60.
- 22 [22] V. Vaiano, G. Iervolino, G. Sarno, D. Sannino, L. Rizzo, J.J. Murcia Mesa, M.C. Hidalgo,  
23 J.A. Navío, *Oil and Gas Science and Technology* 70 (2015) 891-902.
- 24 [23] M. Maicu, M.C. Hidalgo, G. Colón, J.A. Navío, *Journal of Photochemistry and*  
25 *Photobiology A: Chemistry* 217 (2011) 275-283.
- 26 [24] J.B. Hudson, *Surface Science: An Introduction*, Wiley, 1998.
- 27 [25] S. Halas, T. Durakiewicz, *J. Phys.: Condens. Matter* 10 (1998) 10815-10826.
- 28 [26] S. Shen, L. Guo, X. Chen, F. Ren, C.X. Kronawitter, S.S. Mao, *International Journal of*  
29 *Green Nanotechnology: Materials Science and Engineering* 1 (2010) M94-M104.
- 30 [27] V. Vaiano, O. Sacco, D. Sannino, P. Ciambelli, *Appl. Catal., B* 170-171 (2015) 153-161.
- 31 [28] V. Vaiano, G. Iervolino, D. Sannino, L. Rizzo, G. Sarno, A. Farina, *Appl. Catal., B* 160-161  
32 (2014) 247-253.

33

34