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PHOTODEGRADATION OF RHODAMINE 6G IN PRESENCE OF Ag/TiO₂ PHOTOCATALYST

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Abstract

In this work, the commercial titanium dioxide P25 was doped with silver ions via wet impregnation method, in order to improve its catalytic activity. It is already well established that Ag ions can improve the activity of a catalyst and diminish the electron-holes recombination rate. The catalysts obtained by samples calcination at 450 and 600°C were tested as heterogeneous photocatalysts in the degradation of Rhodamine 6G, a very stable fluorescent dye.

The obtained results confirm the improvement of the catalytic activity, compared to TiO₂ P25. Despite the degradation efficiency is not very high, it is worthy to note that the Ag doped catalyst has a higher activity compared to commercial P25. Thus, we can conclude that modifying the catalyst surface leads to an improvement of the properties, probably by forming an intermediate energy level between the valence and conduction bands of TiO₂.

Keywords: *Ag-doped catalyst, photocatalysis, rhodamine degradation, titanium dioxide*

Introduction

The occurrence of organic dyes in water represents an increasing environmental problem due to their high toxicity and, therefore, their consequences on human health (Ciobanu et al 2013, Ciobanu et al 2014, Harja et al 2011, Harja et al 2016, Harja et al 2017, Harja & Ciobanu 2018, Rokesh et al 2018, Rusu et al 2014). The heterogeneous photocatalysis, using metal oxide semi conductive nanoparticles, proven to be one of the most effective "green" techniques for the degradation of organic and inorganic micro-pollutants from wastewater (Favier et al 2016, Wen et al 2015). The most popular semiconductors in this respect are: TiO₂, ZnO, CuO, Fe₂O₃, CeO₂, (Nutescu Duduman et al 2016, 2018, Saleh et al 2016); the first being from far the most promising, due to its high photocatalytic activity, chemical stability, lack of toxicity, low cost, large availability (Wen et al 2015). The performant photocatalysts can mineralize the organic compounds to carbon dioxide, water and simple mineral acids. This mechanism is attributed to the semiconductor's ability to form electron-holes pairs and produce hydroxyl radicals by the reaction occurring between charged carriers and water, under UV light irradiation. Despite these advantages, efforts are still dedicated to TiO₂ activity improvement, by its doping with metal ions (Nakata et al 2012).

The objective of this work was to test the activity of Ag-doped photocatalyst in the degradation of Rhodamine 6G (R_6G), a chemically stable organic dye widely used as a textile dye, water flow tracer, biotechnological applications (various versions of fluorescence microscopy) (Li et al 2018, Lutic et al 2012).

The activity of the doped catalyst was compared to that of the parent P25 (Degussa).

Materials and Methods

TiO₂ P25 Degussa (P25) was used without further purification. Silver nitrate (AgNO₃) used for Ag doping was purchased from Sigma Co.

The Ag/TiO₂ catalyst was prepared by the incipient impregnation method. The P25 powder was dried for 2 hours at 200°C, then the AgNO₃ solution in water and ethanol was added fast, in order to fill the empty pores from the solid structure and allow the uniform Ag dispersion on the whole surface. The sample was cooled at 25°C and dried at 100°C for a few hours. One half of the powder was calcined at 450°C, the other half at 600 °C (1°/min) for 2 hours.

The P25 and synthesized materials were characterized by EDAX, SEM and XRD.

The photocatalytic activity of Ag/TiO₂ was evaluated by the degradation of R_6G, under UV light. The experiments were performed in a batch reactor, magnetically stirred, with internal irradiation, using an Osram UV-A lamp (9W). The tests were carried out at ambient temperature, without adjusting the native pH of the dye.

The working solutions of dye were obtained by diluting accordingly stock solutions prepared in deionized water, by dissolving precisely weighted amount of R_6G. In order to achieve the adsorption-desorption equilibrium, the solution with the photocatalyst powder was first stirred in dark for 30 min, and then the lamp was turned on. The photocatalytic tests were run for 120 min and samples were taken at specific times, filtered through 0.45 µm syringe filters to remove the catalyst and measured. The dye concentration was determined by spectrophotometry, using a Shimadzu UV-1700 spectrophotometer, on the basis of the characteristic R_6G peak from 525nm.

The degradation efficiency was calculated with the following equation:

$$D \% = (C_0 - C_t) / C_0 * 100 \quad (1)$$

where C₀, C_t – initial and respectively time t pollutant concentrations.

Results and Discussion

The samples were analyzed by EDAX analysis in order to determine their chemical composition. The results are shown in Table 1.

Table 1. The EDAX measurement of Ag/TiO₂ 450 °C and 600 °C samples.

Element	Ag, wt%	Ti, wt%
Ag/TiO ₂ 450 °C	9.91	52.17
Ag/TiO ₂ 600 °C	6.79	55.6

From the results, it can be seen that at a higher calcination temperature, the Ag percentage on the catalyst surface decreases and the Ti percentage increases accordingly. This indicates that Ag particles could be removed at a higher temperature.

The obtained catalyst was characterized by XRD to determine the crystalline structure and phase purity. The XRD diffraction patterns reveals that the sample

calcined at 450°C mostly contains anatase phase, while the one calcined at 600°C is composed only of rutile phase, Figure 1. At higher calcination temperature, the anatase phase was almost entirely converted to rutile phase (Sangchay et al 2012).

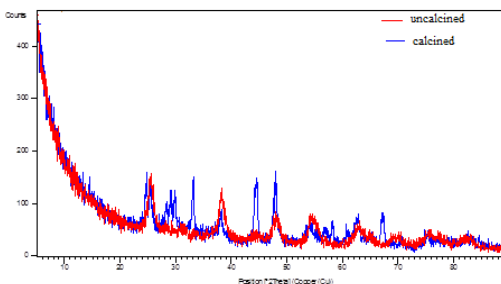


Figure 1. XRD for the Ag/TiO₂ samples uncalcined and calcined at 450 °C

The SEM for samples uncalcined and calcined at 450°C are presented in Figure 2.

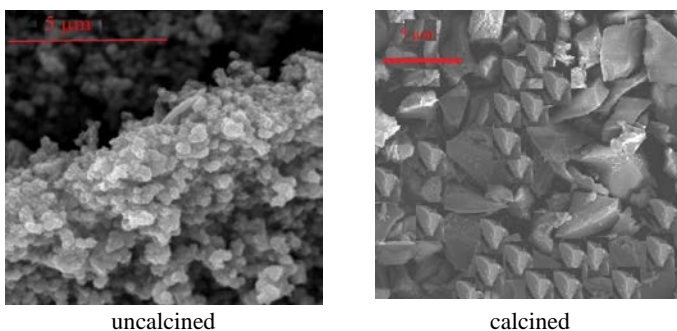


Figure 2. SEM for the Ag/TiO₂ samples uncalcined and calcined at 450°C

The activity of the doped catalyst was investigated by heterogeneous photocatalysis in the degradation of R_6G (chemical formula: C₂₈H₃₁N₂O₃Cl) and compared to that of P25 Degussa.

Ag/TiO₂ calcined at 600°C was totally inactive for the photodegradation of R_6G, since the rutile phase is known to be unsuited for photocatalysis. Therefore, the notation Ag/TiO₂ used from now on refers to the sample calcined at 450°C.

In order to highlight the effect of catalyst loading, we ran tests at a catalyst loading of 0.5 g/L and 1 g/L and a pollutant concentration of 40 mg/L, in the fore-mentioned operatory conditions.

The activity of the catalysts is very low at a catalyst dose of 1g/L (data not shown). This is due to an overload of catalyst which produces a “screening effect”; the aqueous photocatalyst slurry is almost opaque, therefore the irradiation effectiveness decreases (Yoon et al 2012). The other series of tests were carried out at a catalyst loading of 0.5 g/L.

The data in Figure 3 indicate that a degradation of almost 35% was achieved when a R_6G solution of 40 ppm was used. This is a quite high initial concentration for

R₆G, the optical density of the solution hinders in an important extent the radiation to reach the active sites of the catalyst, which are in turn highly covered with multilayers of pollutant molecules (Yang et al 2018).

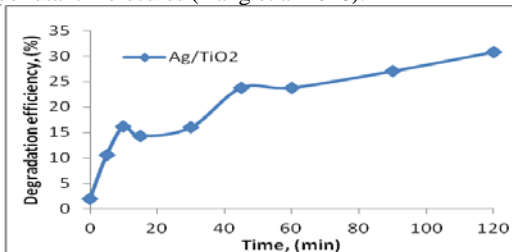


Figure 3. Degradation efficiency of R₆G in presence of Ag/TiO₂. Experimental conditions: [R₆G] = 40 mg/L, [Ag/TiO₂] = 0.5 g/L.

The use of pristine P25 in same photoreaction conditions led to a degradation efficiency of only 23% (Figure 4). These results clearly show that the doping with Ag improved the photocatalytic activity of P25.

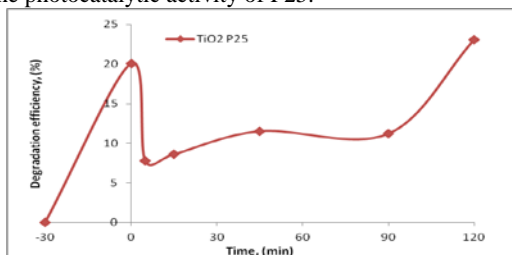


Figure 4. Degradation efficiency of R₆G in presence of P25. Experimental conditions: [R₆G] = 40 mg/L, [P25] = 0.5 g/L.

From the absorbance spectra (Figure 5) it can be seen that the main peak decreases constantly during the photocatalytic reaction, likewise the peak from the UV region. Thus, this indicates that during the reaction, the pollutant molecule is mineralized.

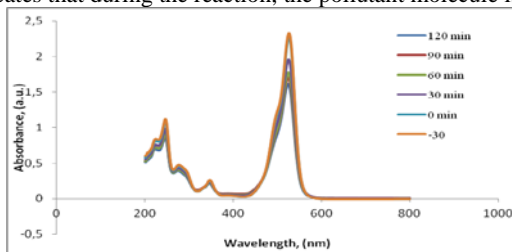


Figure 5. R₆G spectra during the photocatalytic assay. Experimental condition: [R₆G] = 40 mg/L, [Ag/TiO₂] = 0.5 g/L

Conclusions

The results shown that by doping TiO₂ photocatalyst with Ag via wet impregnation method is a promising approach to increase the photocatalytic activity of the semiconductor.

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