EFFECT OF DOPING OF TiO$_2$ NANOPARTICLES WITH SILVER ON THEIR PHOTOCATALYTIC ACTIVITIES TOWARD DEGRADATION OF E 131 VF

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ABSTRACT

Ag-doped TiO$_2$ nanoparticles are prepared by the wet impregnation method with a variable M/TiO$_2$ mole ratio between 0.4 % and 5 %. X-ray diffraction, scanning electron microscopy, FT-IR and Raman spectroscopy techniques are used to characterize the samples. The results show that the rutilation is negligible despite calcinations at 500ºC. The materials catalytic activity in respect to the food colorant E 131 VF photodegradation is evaluated. It is shown that the catalytic system advanced provides E 131 VF degradation with no adsorption on TiO$_2$ surface. In general, the enhancement of TiO$_2$ photoactivity is slight after doping with Ag metal. The enhancement caused by addition of Ag (I) to TiO$_2$ is largely inhibited by the particles agglomeration caused by the impregnation technique.

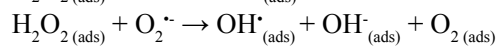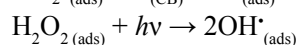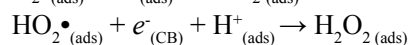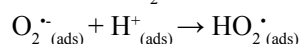*<u>Keywords</u>: Ag/TiO$_2$, E 131 VF, photocatalysis.*

INTRODUCTION

The removal of color from the wastewater coming from different industries is a current issue of discussion and regulation all over the world [1]. Several studies on the physical, chemical and biological degradation of dye containing wastewater have been reported in the literature [2]. A heterogeneous photocatalytic oxidation process has been recently used as a promising technology for the removal of toxic organic and inorganic contaminants from industrial wastewater by completely destroying the organic contaminants to CO$_2$, H$_2$O and mineral acids [3]. TiO$_2$ is broadly used as a photocatalyst because of its nontoxicity, a photochemical stability, and a low cost [4]. When TiO$_2$ is irradiated with ultraviolet (UV) light, an electron is promoted from the valence band to the conduction band resulting in the generation of a positive hole (h$^+$) at the valence band and the release of an electron (e$^-$) in the conduction band. The electrons

and the positive holes can recombine with each other within the crystal. The charges created can react with the adsorbed substances that can accept or donate electrons. Thus, the electrons can reduce an acceptor, while the positive holes can oxidize a donor. The free electrons react with the adsorbed oxygen to form superoxide radical anions (O$_2^{\bullet-}$):

$$O_{2\,(ads)} + e^-_{(CB)} \rightarrow O_2^{\bullet-}{}_{(ads)}$$
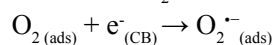
In the presence of adsorbed protons, the superoxide anion can lead to the formation of a hydroperoxide radical (HO$_2^{\bullet}$) and then hydrogen peroxide (H$_2$O$_2$), which can decompose on the catalyst surface to a hydroxyl radical (OH$^{\bullet}$) under the action of radiation, or by reactions with O$_2^{\bullet-}$:

$$O_2^{\bullet-}{}_{(ads)} + H^+_{(ads)} \rightarrow HO_2^{\bullet}{}_{(ads)}$$
$$HO_2^{\bullet}{}_{(ads)} + e^-_{(CB)} + H^+_{(ads)} \rightarrow H_2O_{2\,(ads)}$$
$$H_2O_{2\,(ads)} + h\nu \rightarrow 2OH^{\bullet}{}_{(ads)}$$
$$H_2O_{2\,(ads)} + O_2^{\bullet-} \rightarrow OH^{\bullet}{}_{(ads)} + OH^-{}_{(ads)} + O_{2\,(ads)}$$

while the energized holes react with water (H$_2$O) or

organic compounds to form hydroxyl radicals (OH$^{\bullet}$):

$$H_2O_{(ads)} + h^+_{(VB)} \rightarrow OH^{\bullet}_{(ads)} + H^+_{(ads)}$$
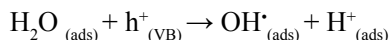
In turn, the generated species (OH$^{\bullet}$, O$_2$$^{\bullet-}$, R$^{\bullet}$) are very reactive and can oxidize the compounds present leading to their mineralization.

The rapid recombination of the electron-hole pair limits also the efficiency of TiO$_2$ because it contributes to the loss of the reactive species cited above. Therefore, the modification of TiO$_2$ aiming to improve its photocatalytic efficiency is one of the most important objectives of the photocatalysts studies [4, 5]. In particular, the noble metal-modified semiconductor nanoparticles have become the focus of many studies aiming to maximize the photocatalytic reactions efficiency. Because the Fermi levels of these noble metals are lower than those of TiO$_2$, the photoexcited electrons can be transferred from the conduction band of TiO$_2$ to the metal particles deposited on the surface of TiO$_2$, while the photogenerated holes in the valence band remain on TiO$_2$ [6]. This reduces greatly the possibility of electron-hole recombination resulting in efficient separation and higher photocatalytic activity. In addition, the photoelectrons can enhance the rate of oxygen photoreduction and favor the generation of hydroxyl radicals, thereby contributing to more effective organic pollutant photoelimination [7]. The effects of silver and palladium on the photocatalytic removal of organic substrates have previously been described in the literature [8-17]. The activity of the metal-modified materials depends on the nature of the organic compound as well as on other factors which include the pollutant concentration, the pH value, the metal type and its load, as well as the adsorption rate of the pollutant [8, 18]. The literature shows that small amounts of silver or palladium on the surface of TiO$_2$ enhance its photoactivity in respect to the decomposition of several pollutants when compared to that of bare TiO$_2$ [8, 9, 12, 15, 16]. However, sometimes the photocatalyst surface modification by deposition of Ag [19, 20] and Pd [21] can have no significant effect on its photoactivity.

The aim of this work is to study the effect of Ag deposits on a TiO$_2$ catalyst type P25 in respect to the photodegradation of the food colorant E 131 VF. The studied catalysts are obtained by wet impregnation of the carrier by AgNO$_3$ solutions of a varying Ag/TiO$_2$ molar ratio between 0.4% and 5%. The effect of the calcinations temperatures on the obtained catalysts efficiency is also considered.

EXPERIMENTAL

Materials and preparation

The TiO$_2$ nanoparticles (P25, ca 80 % of anatase, 20 % of rutile; a particle size of ca 21 nm; BET area of ca. 50 m^2 g^{-1}) were supplied by Sigma Aldrich. The food colorant E131VF was also obtained from Sigma Aldrich (C$_{27}$H$_{31}$N$_2$O$_6$S$_2$-Na, purity of 50 %, MW of 565.67 g). The aqueous stock solutions containing the food colorant were prepared, protected from light, and stored at an ambient temperature. The experimental concentration of the dye was selected so that its absorbance followed the Beer's law (A$_{640}$:1.6). AgNO$_3$ (99 %) was supplied by BDH.

Preparation of the photocatalysts

Ag-doped TiO$_2$ were prepared by the wetness impregnation method according to the procedure described in ref. [2]. Calculated amounts of AgNO$_3$ were added to TiO$_2$ in order to get Ag/TiO$_2$ molar ratio of 0.4 %, 0.8 %, 1 %, 1.2 %, 1.6 %, 2.5 % and 5 %. Then 100 ml of distilled water were added to each sample and stirred for 8 h at a room temperature. After maturation within 12 h, the solutions were dried at 100°C for another 12 h prior to grinding and calcinations (successively at 300°C, 400°C and 500°C) for 4h in a muffle furnace. For comparison purposes, a bare support TiO$_2$ P25 was also ground and calcined under identical conditions in order to be used as a reference sample. The prepared catalysts were named xAg/TiO$_2$y (x and y stood for the Ag/TiO$_2$ molar ratio and the calcination temperature, correspondingly).

Characterization of the photocatalysts

The X-ray diffraction pattern was recorded on D8 Focus, Bruker, X-ray diffractometer operating at 50 kV using Cu-Kα radiation (λ = 1.541 Å). The measurement was performed over a diffraction angle range of 2θ = 5°- 80°. Fourier transform infrared (FTIR) spectroscopy was applied on Jasco FT/IR- 6300 spectrometer in the wavelength range of 400 cm^{-1} - 4000 cm^{-1}. The FTIR

study was performed by using KBr pellet. The Raman spectra were recorded on Horiba Scientific operating with green Laser at 532 nm. The scanning electron microscopy (SEM) images were taken with Ametek materials analysis division (AIS 2300C series) instrument (a working distance of 25 mm, voltage of 20 kV). The EDX spectra were recorded in the binding energy region of 0 keV - 8 keV.

Photocatalysis experiments

All prepared catalysts were grinded with an agate mortar before the photoactivity investigation. Prior to illumination commencement, a suspension containing 0.08 g of the catalyst and 100 mL of an aqueous solution of E 131 VF were stirred continuously for at least 15 min in dark. Then the sample was irradiated under magnetic stirring by two UVB lamps (λ_{max} 320 nm) positioned at 10 cm above the glass bowl (a photoreactor from Luzchem LZC-4V, Canada). To quantify the decrease of the food colorant concentration with time, a sample of 3 ml was taken (with a pipette) at predetermined intervals of time and centrifuged at 4000 rpm for 10 min in order to be analyzed by a double beam UV-visible spectrophotometer measuring the absorbance at the maximum wavelength of E 131 VF (640 nm).

RESULTS AND DISCUSSION

Catalysts characterization

The XRD diffraction patterns of calcined P25, Ag doped TiO_2 show five primary peaks at 25.3°, 38°, 48.2° and 62.5° which can be attributed to different planes of pure anatase. Other peaks at 27.36°, 36°, 54° and 69° can be referred to pure rutile form of TiO_2 (P25) [22]. The anatase reflections are dominating in the reflection patterns but rutile is also present as the original material (TiO_2, P25) contains both phases. The strongest peak at $2\theta = 25.3$° is representative for (1 0 1) anatase phase reflections (Fig. 1). These results show that the XRD patterns of all solids almost coincide with that of the original material P25, which is an indication that the structural integrity of the support is retained after metal doping [23] under the work conditions used.

It is seen that the calcination temperature increase up to 500°C does not significantly increase the effect of rutilation. Furthermore, there are no obvious peaks showing the presence of silver in the XRD samples even at Ag/TiO_2 molar ratio of 7.5 %. This indicates that the Ag particles are well dispersed on TiO_2 surface. Hence, these metal sites are expected to be below the visibility limit of X-ray analysis.
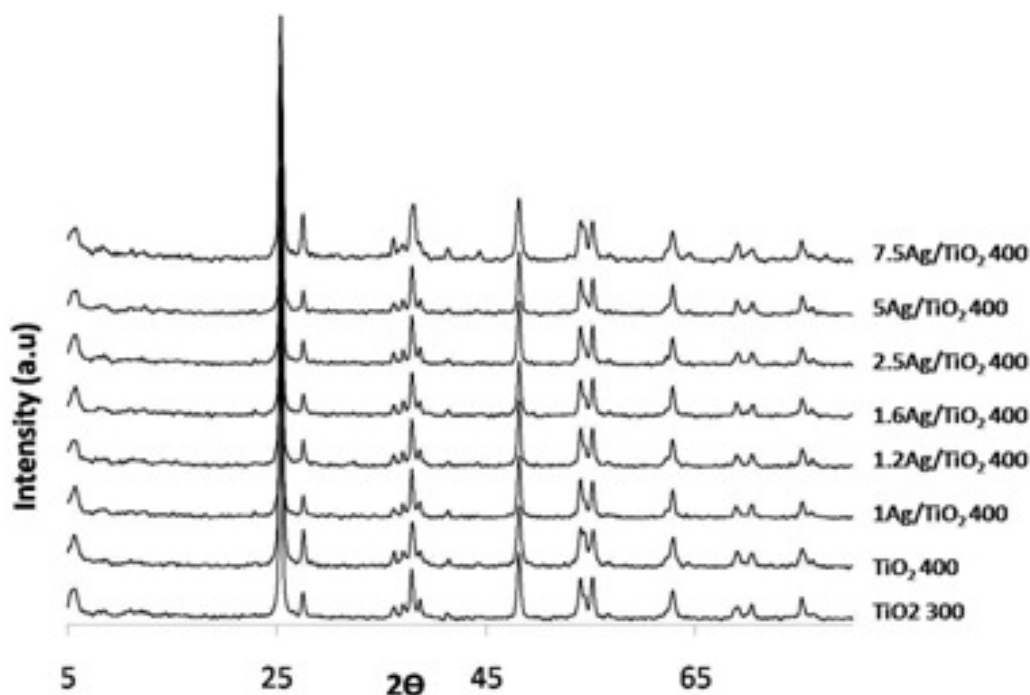

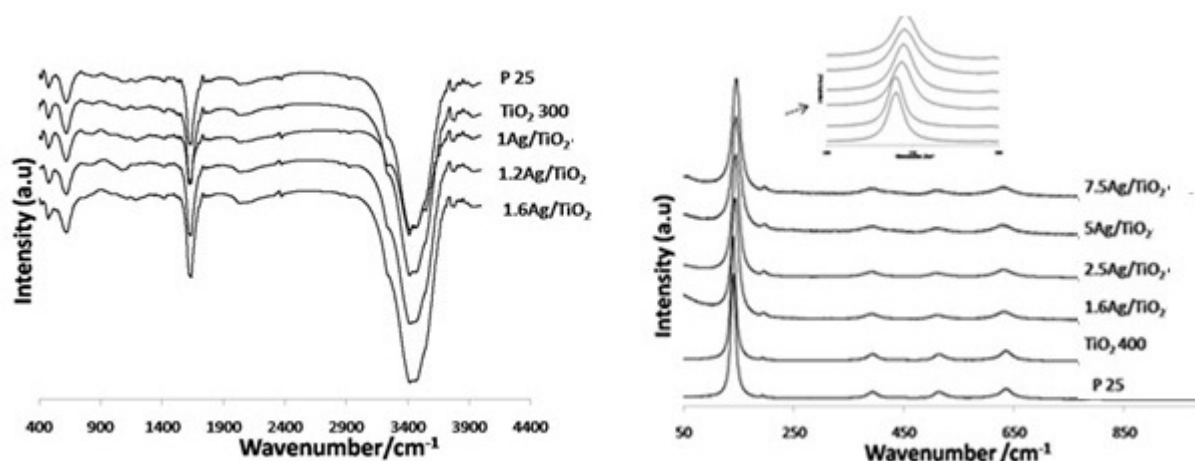Fig. 1. XRD patterns of the calcined TiO_2 and Ag/TiO_2.

Fig. 2a. FTIR spectra of P25, the calcined TiO_2 and Ag/TiO_2 calcined at 400°C.
Fig. 2b. Raman spectra of P25, the calcined TiO_2 and Ag/TiO_2 calcined at 400°C.

The FTIR spectra of Ag/TiO_2 show that all solids present FTIR spectra almost similar to that of P25; the peaks observed at 476 cm^{-1} and 620 cm^{-1} are assigned to the vibrations of Ti–O and Ti–O–Ti framework bonds of TiO_2 [24]. The broad peaks at 3420 cm^{-1} and the peak at 1620 cm^{-1} are characteristic of the H–O bending mode of the hydroxyl groups present on the surface of the catalyst due to moisture (Fig. 2a). As the amount of Ag salt added is small, no new band and no shift are observed in the bands of bare TiO_2 after doping. This supports the fact that an efficient dispersion of the doping ion is achieved.

The Raman spectra (Fig. 2b) show that both P25 and calcined TiO_2 powders are in an anatase phase [25]. Besides, no secondary peaks related to the doped metals or their oxide phases are detected. This fact is in an agreement with the XRD and FTIR results obtained. The position of the Raman bands near 144 cm^{-1} shifts towards higher wavenumbers with increase of Ag/TiO_2 molar ratio. Such phenomenon has already been observed by Choudhoury et al. [26] who report broadness and shifting to a higher wavenumber in case of Cu loading of TiO_2 nanoparticles. They suggest that this
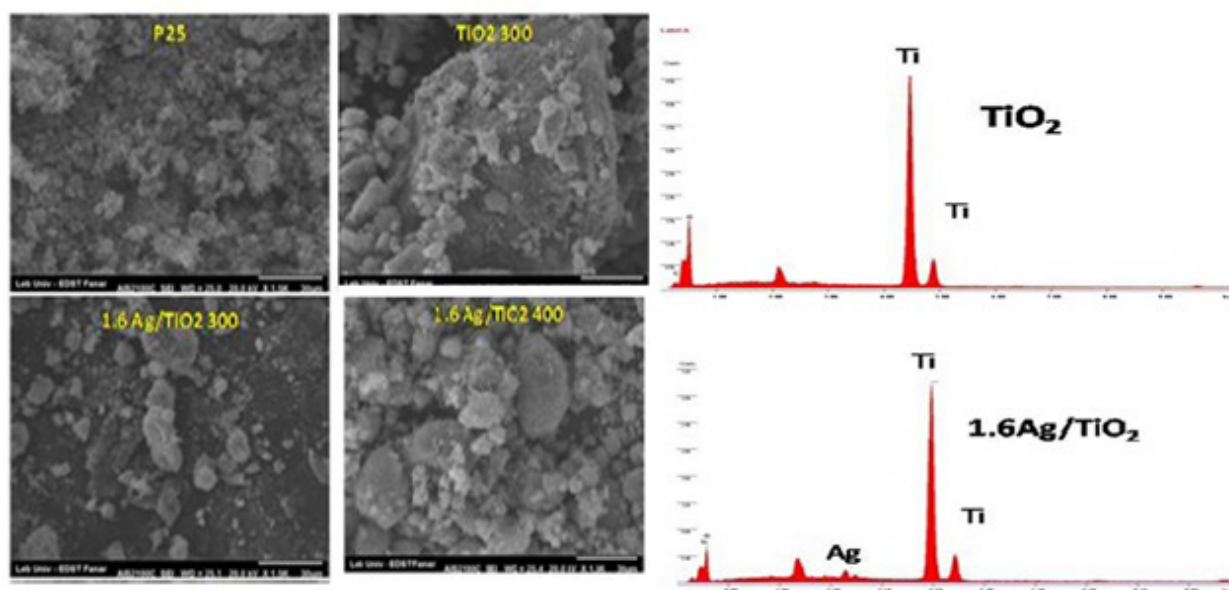

Fig. 3a. SEM images of P25, the calcined TiO_2, and 1.6 % Ag/TiO_2.
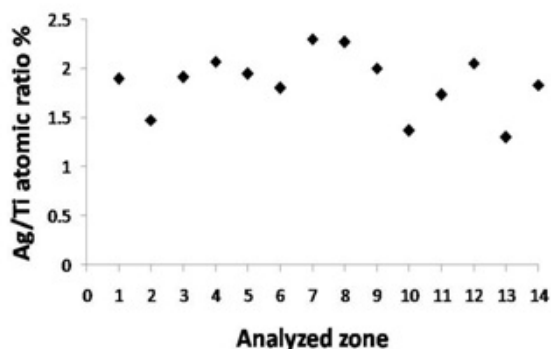Fig. 3b. EDX spectra of TiO_2 300 and 1.6 % Ag TiO_2 300.

Fig. 4. Variation of the 1.6 Ag/TiO$_2$ % ratio as function of the zone analyzed.

phenomenon is related to the doped metals ionic size. The doping of Cu^{2+} of an ionic size (0.73 Å) larger than that of Ti^{4+} (0.64 Å) contributes to the distortion of the lattice structure of TiO$_2$ and the formation of O$_2$ vacancies. Their explanation can be taken into consideration in view of the fact that Ag$^+$ has an ionic size of 1.26 Å, which is larger than that of Cu^{2+}. Parker and Siegel show [27] that the oxygen vacancies are responsible for the shifting and the broadening of the Raman peak.

The SEM images of the original pure TiO$_2$ P25, the calcined TiO$_2$ and the 1.6 % Ag doped catalysts calcined at 300°C and 400°C are presented in Fig. 3a. The typical SEM images show that pure TiO$_2$ P25 has uniform and smooth particles. They increase in size after TiO$_2$ treatment at 300°C due to agglomeration. The presence of Ag does not contribute to significant modifications of the morphology and the particle size of TiO$_2$ calcined

at 300°C. However, the increase of the calcination temperature from 300°C to 400°C increases further, although slightly, Ag/TiO$_2$ particles size.

The EDX spectra confirm the presence of Ag in the doped catalysts (Fig. 3b). For both catalysts, the intense peak at 4.51 keV is assigned to bulk TiO$_2$, while the less intense one is attributed to surface TiO$_2$ [28, 29]. The peak of Ag is located at 2.9 keV. Sixteen zones of 1.6 Ag/TiO$_2$ are analyzed. The ratio of Ag/TiO$_2$ % varies between 1.4 and 2.4, which means a uniform distribution of iron on TiO$_2$ (Fig. 4).

Photocatalytic activity

The photocatalysis experiments take place in an aqueous solution of the food colorant to evaluate the effect of doped Ag on TiO$_2$ activity. The photocatalytic activity of all solids is evaluated on the ground of the time variation of E 131 VF absorption at 640 nm (λ_{max}).

Blank experiments are carried out (i) in absence of a photocatalyst under UV irradiation and (ii) on a bare P25 support in dark to verify E131 adsorption on TiO$_2$.

In absence of a photocatalyst, the absorbance decreases nearly 10 % after UV irradiation for 30 min (13 % after 2 h, 20 % after 4 h). So there is a negligible degradation of E131 in absence of a catalyst. In presence of a bare P25, the absorbance value of the food colorant solution after stirring in dark for 20 min (and even longer) decreases little (< 6 %) which shows that E131 is very weakly adsorbed on the surface of P25 TiO$_2$.

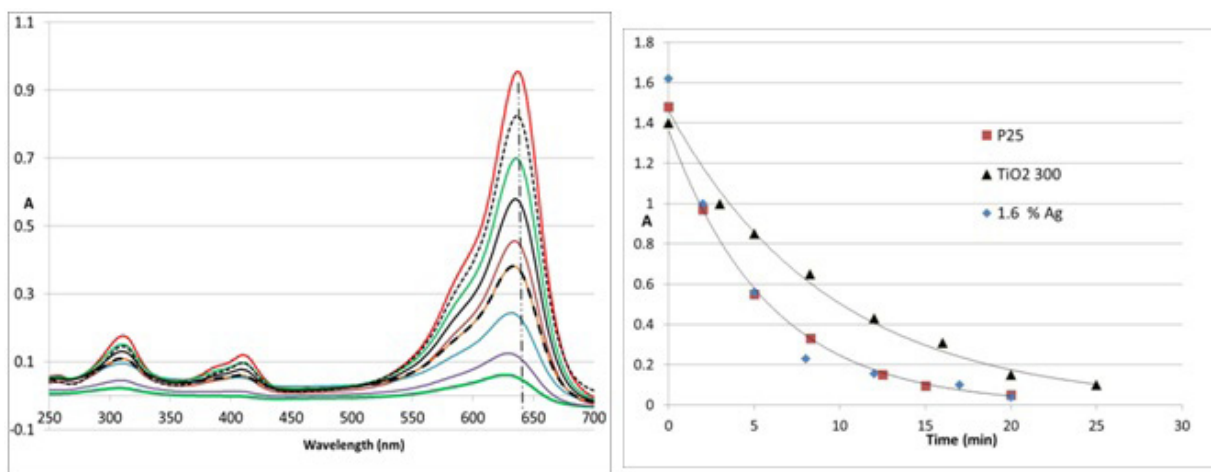**Fig. 5a.** Variation of the UV-Visible spectrum during the photocatalytic degradation of E 131 VF in the presence of TiO$_2$ (P25).
Fig.5b. Variation of the A$_{640}$ as function of time in the presence P25, TiO$_2$ 300 and 1.6 Ag/TiO$_2$300.
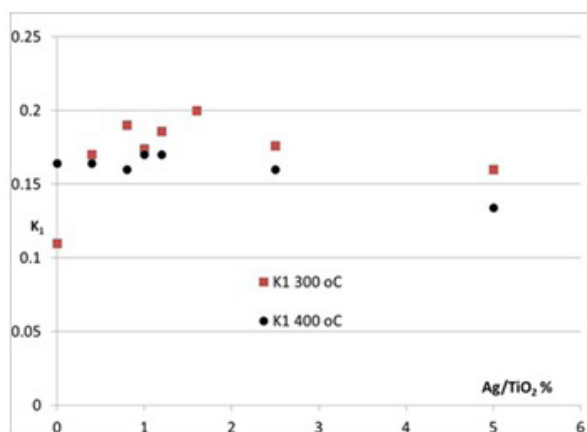
Fig. 6. Variation of the rate constant K_1 (min^{-1}) as function of the Ag/TiO$_2$ %.

However, in presence of both P25 catalyst and UV irradiation, there is a fast decrease of A_{640} which means a fast degradation of E 131 VF. This highlights the importance of using TiO$_2$ photocatalyst (k1: 0.17 min^{-1} - 0.18 min^{-1}). Furthermore, as the adsorption of E 131 VF on P25 is negligible, it can be accepted that the photodegradation of the colorant can occur (in absence of adsorption phenomenon of the food colorant on TiO$_2$ surface) in the solution, i.e. in the zone around the photocatalyst particles through interactions with different radicals such as OH•, O$_2$•- and R•. There is a decrease of the whole spectrum during the experiment. A_{max} of E131 shows a slight hypsochromic shift during the photodegradation (Fig. 5a). No new absorption bands appear in the UV-Vis spectrum of the colorant. This result is in accordance with that obtained by Chen [30].

The kinetic study of the degradation of E 131 on Ag/TiO$_2$ samples is illustrated in Figs. 5 and 6. The results show that the process of P25, calcined TiO$_2$, and Ag doped TiO$_2$ catalysts follows the pseudo first order (Fig. 5b). A similar order value is obtained with the samples treated at 400°C and 500°C.

There is a slight increase of the photocatalytic performance of Ag/TiO$_2$300 samples (k$_1$: 0.16 to 0.2 min^{-1}, see Fig. 6) when compared to that of the calcined undoped TiO$_2$ 300 (0.1min^{-1} - 0.11min^{-1}) (Fig. 5). But the further increase of Ag/TiO$_2$ molar ratio up to 7.5 % results in a considerable efficiency decrease (the result is not shown). The recalcinations of the same catalysts at a higher temperature (400°C) do not show any significant

change of the catalysts activity. I.M. Arabatzis et al. [31] report that the decrease of Ag/TiO$_2$ efficiency with increase of Ag$^+$ ion concentration is due to shading of the available semiconductor surface by the silver layer.

In most studies, the authors ascribe the catalytic performance to the adsorption factor of the pollutant on the catalyst [8, 20]. For example, the study of Hoang Tran et al. [8] shows that the silver deposits have a negligible effect on the mineralization of the organic compounds. They report that the alcohols do not benefit by the presence of silver due to their limited adsorption on TiO$_2$.

Moreover, the active part of a photocatalyst is its illuminated zone being in contact with the organic pollutant [31]. As P25 particles are smooth and soft, they are well dispersed in the liquid reaction medium, which in turn increases the surface area available for photon absorption and subsequent free radicals liberation. But in case of Ag/TiO$_2$ samples, the particles agglomerate. This may explain their slight sedimentation even with stirring and their poor dispersion in the solution. This phenomenon abates the illuminated surface of the metal doped catalysts in comparison to that of P25 and as a result decreases the amount of the free radicals responsible for the degradation of E 131VF in the solution. Khaki et al. [32] show that there is an optimal temperature for doped-TiO$_2$ calcination beyond which the photocatalytic activity may be reduced due to particles agglomeration decreasing the specific surface area of the photocatalyst. Thus, the present work focused at the photocatalytic degradation of E 131 VF in an aqueous suspension explains the slight increase of Ag/TiO$_2$ catalyst photoactivity by the presence of two opposite phenomena:

The presence of Ag on the surface of TiO$_2$ decreases the recombination rate of e$^-$ - h$^+$ leading to an increase of the bare catalyst photoactivity.

The agglomeration of Ag/TiO$_2$ particles upon calcination results in a decrease of the area exposed to radiation, and consequently in a decrease of the active radicals produced.

CONCLUSIONS

The present work describes the preparation of Ag/TiO$_2$ catalysts by impregnation and the study of the effect of TiO$_2$ doping on the photocatalytic

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degradation of E 131 VF. The catalysts calcination at 300°C and 400°C contributes to a significant agglomeration of the particles of the bare and doped TiO$_2$, whose size increases unlike the uniform and smooth particles of pure TiO$_2$ P25 Degussa. It is found that the samples containing a small amount of Ag/TiO$_2$ have a slight positive effect on the photocatalytic activity of TiO$_2$ when treated at 300°C. It is also found that the photodegradation of the colorant can occur not through adsorption phenomena on TiO$_2$ surface but in the solution by interaction with the different radicals produced. The catalytic results obtained provide the suggestion that in a liquid suspension reaction medium there is a close relationship between the particles size of the catalyst (which maintains its dispersion in the reaction medium) and the degradation rate of the pollutant. The addition of Ag to TiO$_2$ does not present an important positive effect with respect to the catalytic performance of P25 due to the problem (agglomeration) caused by the impregnation method.

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