Original Article

Synthesis and characterization of silver-titania nanocomposites prepared by electrochemical method with enhanced photocatalytic characteristics, antifungal and antimicrobial activity

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**A B S T R A C T**

The paper deals with the synthesis of silver-titania (Ag-TiO$_2$) nanocomposites with enhanced photocatalytic, antifungal and antimicrobial characteristics. Ag nanoparticles have been electrochemically deposited on the commercially available nano-TiO$_2$ powders involving the so-called "sacrificial anode" technique. The obtained nanocomposites were characterized by X-ray diffraction, XPS and Raman spectroscopy to get information on their composition and structure. Particle size distribution and stability of Ag-TiO$_2$ based colloidal solutions have been determined from dynamic light scattering and zeta potential measurements. The recorded UV–vis diffuse reflectance spectra evidenced the presence of an absorption band located in the range of 475–525 nm and the presence of a tail as well, suggesting a better photocatalytic activity. The photoreactivity of the synthesized Ag-TiO$_2$ nanocomposite as well as the influence of Ag content were evaluated for the degradation of Orange II dye under UV irradiation ($\lambda$ = 365 nm). The heterogeneous photocatalytic degradation rate follows pseudo first order kinetics. Antifungal and antimicrobial efficacy evaluation showed that the synthesized Ag-TiO$_2$ nanocomposites are significantly more active than pure titania.

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1. Introduction

In the last years, semiconductor oxides, including TiO$_2$, are used as photocatalyst to oxidize and decompose a wide range of organic and inorganic compounds, also having antibacterial effect. Under UV light irradiation, TiO$_2$ is a very efficient photocatalyst because electrons and photogenerated gaps are strong oxidizing agents and, respectively, reduction agents. However, it is inactive under the action of visible light due to its large band gap (3.0–3.2 eV), which makes it unable to use the huge potential of solar photocatalysis. The modification of TiO$_2$ to render it sensitive to visible light is one of the most important goals to enable its increased utility.

Currently, research focuses on achieving a highly efficient photocatalytic action of these materials under visible spectrum light as well, through various functionalization techniques to make them absorb photons at a lower energy; these techniques include surface modification, therefore forbidden energy band modifications by creating oxygen vacancies and sub-stoichiometric oxygen by doping/co-doping with non-metals and/or metals [1–3].

The presence of the doping ions within the titania structure caused significant absorption shift to the visible region compared to pure TiO$_2$ powder. Highly active radical species, produced at TiO$_2$ surface under UV/visible light irradiation participate in oxidation reactions, thus facilitating the destruction of organic contaminants and also causing microorganism's inactivation [1,3,4].

Many studies have been performed to develop titania with a good response under visible light by doping it with various non-metals as a substitute for oxygen in the TiO$_2$ lattice. For these non-metal-doped TiO$_2$ photocatalysts, the mixing of the p-type states of the doped non-metal (N, S or C) with the O 2p states shifts the valence band edge upwards, narrowing the band gap energy of TiO$_2$ [2,5,6].

In order to avoid the recombination of the charge carriers of the photoexcited TiO$_2$, i.e., electron–hole (e$^–$–h$^+$) pair, besides non-metals the noble metals (e.g., Ag, Au) addition may enhance its overall photocatalytic efficiency. The noble metal deposited on TiO$_2$ becomes a high Schottky barrier and thus acts as electron trap, facilitating electron–hole separation and promoting the interfacial electron transfer process [7]. The metal–TiO$_2$ composites show a lower e$^–$–h$^+$ recombination rate than the pure TiO$_2$, because the electrons accumulate on the metal and the holes remain on the photocatalyst surface, so that a better charge separation occurs. Moreover, surface plasmon resonances of noble metal particles, which can be excited by visible light, increase the electric field around metal particles and thus enhance the surface electron excitation and electron–hole separation on noble metal-deposited TiO$_2$ [8].

Einaga [9] showed that Ag deposition on TiO$_2$ surface is effective to improve the catalytic activity of TiO$_2$ and the highest reaction rate was obtained at the loading level of 2.0 wt.% Ag, when the rate was 4.0 times larger than that of pure TiO$_2$. Moreover, it was reported that noble metals additions, especially silver, could degrade the pathogen microorganisms, showing strong biocidal effects on a large spectrum of bacteria species including Escherichia coli [10–12]. It is generally believed that silver can bind to bacterial cell wall membrane and can damage it, altering its functionality. Because of the interaction between the silver and bacterial DNA structure, their multiplication may be prevented [13]. According to this mechanism, silver can prevent the growth of a broad variety of microorganisms such as molds, viruses and bacteria, as reported previously [12–14].

Stoimenov and co-workers demonstrated that highly reactive metal oxide nanoparticles exhibit excellent biocidal action against Gram-positive and Gram-negative bacteria [15]. Thus, the preparation, characterization, surface modification and functionalization of nano-sized inorganic particles open the possibility of formulation of a new generation of bactericidal materials. Nano silver-deposited on nano TiO$_2$ with high surface area has a great potential for antibacterial and antifungal applications because the release of silver ions can be delayed for a long time, if silver is immobilized on porous hosts [16,17]. Liu et al. have showed that Ag/TiO$_2$ composites present a strong germicidal action in visible light [18]. Currently, fungal growth is a critical issue for a large range of materials, including leather, epoxy polymers, ceramics. The commercial fungicides exhibit a high level of toxicity so that the development and use of novel more environmentally friendly nanomaterials represent a promising expectation.

The most applied procedures to dope titania are based on chemical techniques. Here we report an innovative electrochemical based synthesis to produce Ag–TiO$_2$ nanocomposites [19]. Efficiency in the improvement of the photocatalytic activity in both UV and visible-light was demonstrated through diffuse reflectance spectra (DRS) and photocatalytic tests. Antifungal/antibacterial evaluation of the obtained Ag–TiO$_2$ as nano dispersions, slurry and powders has been also performed.

2. Experimental

2.1. Chemicals and materials

All used chemicals, respectively: sodium polyacrylate (Na-PAA), Orange II dye, were of analytical grade and supplied by Sigma Aldrich. TiO$_2$ nanopowder of 99.5% purity was supplied by TitanPE Technologies, Inc., China (particle size of max. 20 nm, surface area of 115 m$^2$/g, and average pore size of 130 Å). The used deionized water had a resistivity of 18 μΩ cm.

2.2. Electrochemical synthesis of Ag–TiO$_2$

Ag–TiO$_2$ composite has been electrochemically prepared involving the so-called “sacrificial anode method” [14,19]. Stable dispersions of 3–10 g/L TiO$_2$ and 0.15–1 g/L Na-PAA in deionized water were used as electrolyte. An inexpensive two-electrode set-up has been involved, both electrodes consisting in 99.999% purity Ag plates (155 × 27 × 0.5 mm). Current densities between 0.01 and 0.06 mA cm$^{-2}$ have been applied for 2–8 h supplied by a constant current pulse reversed generator equipped with a mechanical stirrer (GMC01H-2 type with...
2.3. Characterization

The composition and structure of the nanosized pure TiO₂ and Ag doped TiO₂ powders have been investigated using an X-ray diffractometer Bruker AXS D8 ADVANCE instrument (employing Cu anode and k, Ni filter). Raman spectroscopy was conducted at room temperature using a Horiba LabRam HR 800 instrument, in which the excitation was made by 633 nm wavelength laser light (He–Ne laser).

X-ray photoelectron spectroscopy (XPS) measurements have also been performed involving a Quantera SXM instrument, with a base pressure in the analysis chamber of 10⁻⁹ Torr and an Al Kα radiation (1486.6 eV, monochromatized) as X-ray source. The overall energy resolution was 0.65 eV, determined by the full width at half maximum (FWHM) of the Au4f7/2 line. The spectra have been calibrated using the C1s line (BE = 284.8 eV, C–C (CH)ₙ bondings) of the adsorbed hydrocarbon on the sample surface. A dual beam neutralizing procedure (e⁻ and Ar⁺ ion beams) was applied to compensate for the charging effect in insulating samples.

The nanopowders morphology and composition was analyzed by scanning electron microscopy (SEM) associated with energy dispersive X-ray spectroscopy (EDX) (SU8230, HITACHI High-Technologies Corporation, Japan) and by scanning transmission electron microscopy (STEM) (HITACHI HD-2700). The powdered samples were dispersed in ethanol, sonicated for 1 min and deposited on lacey carbon films coated copper grids. High resolution transmission electron microscopy (HRTEM) and high angle annular dark field (HAADF) images were recorded and analyzed.

Particle size distribution and stability of the prepared Ag-TiO₂ based colloidal solutions were determined by DLS (dynamic light scattering) and zeta potential measurements using a Zetasizer Nano ZS Malvern instrument.

Diffuse reflectance spectra (DRS) were recorded from 200 to 700 nm on dry nanopowder samples using a JASCO 570 UV-VIS spectrophotometer with an integrating sphere. Silver content of composite powder was determined by atomic absorption spectroscopy (AAS) involving a NOVA A 300 instrument after dissolution of the samples in 40% HF solution. Atomic spectroscopy standards were used for calibration.

2.4. Photocatalytic experiments

Comparative photocatalytic activity of Ag-TiO₂ and pure TiO₂ has been evaluated for the degradation of Orange II dye (4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid) under UV irradiation (λ = 365 nm), using a VL 204 UV lamp and under visible light illumination using a 150 W Hg lamp. An amount of 0.0125 g catalyst nanopowder was added into 25 mL Orange II solution having a concentration of 20 ppm. The reactant aqueous suspension was irradiated by the UV lamp or visible lamp under continuous and constant stirring. Prior UV or vis illumination, the suspension was subjected to stirring in the dark for 30 min to reach the equilibrium sorption of the Orange II compound. The absorbance of the dye solution was periodically measured at λ = 484 nm to determine the photodegradation efficiency. The liquid aliquots were passed through 0.1 μm filtering membranes to remove TiO₂/Ag-TiO₂ nanoparticles before spectrophotometrical measurement.

2.5. Antimicrobial activity

2.5.1. Antifungal activity

To evidence fungitoxic properties, the antibiogram method was used [20], involving a fungi mix containing Aspergillus niger, Aspergillus terreus, Aspergillus flavus, Chaetomium globosum, Mirothecum verrucaria, Paecilomyces variotii, Aureobasidium pullulans, Penicillium cyclopium, Penicillium funiculosum, Penicillium glaucum, Trichoderma viride, Scopulariopsis brevicaulis, and Stachybotris atra. According to this method, the fungitoxic effect is expressed by the presence and magnitude of inhibition area for mold growth around the filter paper padded with the tested compounds as solutions and slurries, after different periods of exposure.

2.5.2. Antibacterial activity

The antibacterial activity of Ag-TiO₂ composites was assessed through evaluation of the minimum inhibitory concentration (MIC), defined as the lowest concentration of silver inhibiting completely bacteria growth after 18-24 h of incubation at 37 °C. The samples in the form of colloidal solutions were tested against Staphylococcus aureus (ATCC 6538) as Gram-positive coccobacillus and Pseudomonas aeruginosa (ATCC 9027) and E. coli (ATCC 8789) as Gram-negative cocci, according to the scheme of Ericsson and Sherris [21] involving agar dilution technique. The inoculum was prepared by adjusting the 0.5 McFarland standard and diluting 0.5 McFarland suspension so that the final inoculum was 10⁵ UFC/mL. Nanoparticles-free spots with medium and cultures were used as growth controls.

3. Results and discussion

3.1. Electrochemical synthesis

A relatively simple procedure has been optimized and then applied to electrochemically prepare Ag-TiO₂ nanocomposites, as colloidal solutions or solid nanopowders, as illustrated in Fig. 1.

TiO₂ based aqueous solutions used as electrolytes for obtaining the final Ag-TiO₂ composite have to be stable and well dispersed before the electrochemical step. Usually, polyelectrolytes, their salts or co-polymers are involved as dispersing agents, providing both steric and electrostatic stabilization [22–24].

Based on previous experiments (not shown here) involving measurements of zeta potential and particles size distribution for various compounds, Na-PAA has been selected as dispersant agent able to facilitate formation of stable and well dispersed nano-TiO₂ solutions, which are then used as electrolytes to obtain the final composite.

The optimum Na-PAA concentration was found to be between 0.15 and 0.5 g/L. Fig. 2 presents an example of the recorded particles size distribution and zeta potential for a disperse solution containing 10 g/L TiO₂ and 1 g/L Na-PAA.
The DLS histogram from Fig. 2a evidenced a relatively narrow particle distribution and the zeta potential value of $-45.08 \text{ mV}$ suggested the formation of a quite stable dispersion. Usually, for all investigated disperse solutions having previously mentioned compositions, zeta potentials were situated in the range from $-44 \text{ mV}$ to $-68.2 \text{ mV}$.

The electrochemical step has been applied for different durations and current density values, in order to prepare Ag-TiO$_2$ composites with various silver concentrations. The dependence of Ag concentration within Ag-TiO$_2$ composite against electrolysis time and applied current density for several TiO$_2$ containing disperse solutions is presented in Table 1.

As expected, the silver content increased for longer electrolysis periods, at a constant applied current density. A slight decrease tendency of the Ag concentration is, however, evidenced as the applied current density increased. This behavior might be related either by a possible passivation of Ag electrode or due to a migration of polycrystalline anions that may then hinder the release of silver species.

The final obtained Ag-TiO$_2$ composite based disperse solutions usually had cream colored with yellowish hues, dependent upon the silver content.

### 3.2. Characterization

An example of comparative powder X-ray diffractograms of TiO$_2$ and Ag-TiO$_2$ composite having 2.29 wt.% Ag is shown in Fig. 3. The composite powder was extracted after centrifugation and drying from Solution No. 3, subjected to electrolysis for 2 h at 0.064 mA cm$^{-2}$.

The analysis of the observed peaks for TiO$_2$ sample confirmed the presence of the homogeneous tetragonal anatase crystalline phase (according to ICDD File No. 03-065-5714). The Ag-TiO$_2$ diffractogram also showed the peaks attributed to anatase. Additionally, the Ag-TiO$_2$ pattern exhibited low intensity peaks at $2\theta$ values of $44.5^\circ$, $64.6^\circ$ and $77.5^\circ$ corresponding to (200), (220) and (311) planes of Ag (according to ICDD File No. 04-0783). It was proved that the presence of Ag did not cause changes in the TiO$_2$ anatase crystalline structure.

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**Fig. 1** – Ag-TiO$_2$ electrochemical synthesis procedure.

**Fig. 2** – DLS histogram (a) and zeta potential (b) for a disperse solution containing 10 g/L TiO$_2$ and 1 g/L Na-PAA.
Table 1 – Ag concentration within Ag-TiO₂ composite in the disperse solution as a function of applied current density and electrolysis time.

<table>
<thead>
<tr>
<th>Solution no.</th>
<th>Components concentration in the electrolyte, g/L</th>
<th>Current density, mA cm⁻²</th>
<th>Electrolysis duration, h</th>
<th>Ag concentration, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO₂: 3.5</td>
<td></td>
<td>2</td>
<td>41–42</td>
</tr>
<tr>
<td></td>
<td>Na-P AA: 0.15–0.25</td>
<td>0.016</td>
<td>4</td>
<td>65–66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>91–94</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>115–118</td>
</tr>
<tr>
<td>2</td>
<td>TiO₂: 3.5</td>
<td></td>
<td>2</td>
<td>35–37</td>
</tr>
<tr>
<td></td>
<td>Na-P AA: 0.15–0.25</td>
<td>0.032</td>
<td>4</td>
<td>63–66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>90–93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>100–102</td>
</tr>
<tr>
<td>3</td>
<td>TiO₂: 3.5</td>
<td></td>
<td>2</td>
<td>29–31</td>
</tr>
<tr>
<td></td>
<td>Na-P AA: 0.15–0.25</td>
<td>0.064</td>
<td>4</td>
<td>55–59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>89–91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>85–89</td>
</tr>
</tbody>
</table>

The observed Raman peaks of TiO₂ and Ag-TiO₂ composite match quite well with each other. A sharp and intense peak at 144 cm⁻¹ was evidenced and the further peaks at 197, 397, 519 and 640 cm⁻¹ in the TiO₂ [26,27] exhibited a slight shift in the case of Ag-TiO₂ sample, caused by its smaller crystallite size. These results are in agreement with [14] and confirmed the doping of TiO₂ with silver.

The composition of the electrochemically synthesized Ag-TiO₂ nanopowders has been also investigated involving XPS. Fig. 5 presents the typical XPS survey spectra of the Ag-TiO₂ sample and the corresponding high resolution XPS spectra of Ti2p and Ag 3d.

The wide-scan XPS spectrum for Ag-TiO₂ (Fig. 5a) showed only Ti, O, Ag and C elements with sharp photoelectron peaks appearing at binding energies of 459 (Ti 2p), 530 (O 1s), 368 (Ag 3d) and 285 eV (C 1s), respectively. The carbon peak is attributed to the residual carbon from the sample and adventitious hydrocarbon from XPS instrument itself. The high resolution spectrum of Ti 2p (see Fig. 5b) clearly shows the two characteristic maxima of Ti⁴⁺, at 459 eV (Ti 2p3/2) and 465 eV (Ti 2p1/2) [28,29]. In the Ag 3d XPS spectrum presented in Fig. 5c two peaks at binding energies of 368 eV (Ag 3d₅/₂) and 374.2 eV (Ag 3d₃/₂) are noticed. They correspond to those assigned to metallic silver [30,31], suggesting that the Ag in Ag-TiO₂ is mainly in the metallic state, being consistent with the XRD results.

Fig. 6a and b presents SEM micrographs of an electrochemically synthesized Ag-TiO₂ nanopowder, evidencing distinct particles of nanometric sizes.

By using semiquantitative energy dispersive X-ray spectroscopy (EDX), (see Fig. 6c) the peaks denoting the presence of silver were identified.

A very low peak ascribed to Al element has been detected, probably related to the specimens’ manipulations during SEM investigation. The presence of C and Na amounts evidenced in the spectrum most probably originate from the Na-PAA traces involved during electrochemical synthesis.

Spatially resolved X-ray spectra for a given sample position allowed to evaluate the distribution profiles of elements within the nanopowder. Fig. 7 presents an example of the spatial distribution profiles for the main elemental components. These maps are combined with SEM picture in order to

The average crystallite sizes (d) of the TiO₂ and Ag-TiO₂ samples were determined by analyzing the most intense (101) XRD peaks and using the well-known Scherrer’s equation:

\[ d = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( \lambda \) is the X-ray wavelength, \( \beta \) the diffraction angle and \( \theta \) the half width at half height for the diffraction peak.

The obtained value of average crystallite size of the TiO₂ anatase sample was 16.1 nm and of Ag-TiO₂ composite was 15.6 nm. The slight decrease of the crystallite size in the presence of Ag is in agreement with literature [16,25] confirming that silver presence may suppress the anatase titania crystals growth. Moreover, the use of ultrasound stirring during electrochemical synthesis procedure may also lead to smaller particles, as was also reported in [26] for TiO₂-Pd and TiO₂-Fe systems.

Raman analysis of both TiO₂ and Ag-TiO₂ (2.29 wt.% Ag) powders was attempted in the range from 50 to 1000 cm⁻¹, as exemplified in Fig. 4.
visualize their distribution in the obtained nanocomposite. This analysis suggests a quite uniform distribution of Ag on the TiO₂ surface.

The TEM analysis (Fig. 8) confirms the formation of quite distinct silver nanoparticles. As HRTEM images show (Fig. 8a and c), they have a relatively spherical shape and exhibit a slight degree of agglomeration. In the HAADF–STEM mode (Fig. 8b and d), silver nanoparticles having diameter ranging from 10 to 15 nm can be observed.

Fig. 6 – SEM micrographs at different magnifications (a, b) and EDX spectrum (c) of Ag-TiO$_2$ (1.12 wt.% Ag) nanopowders.

![SEM micrographs](image)

Fig. 7 – SEM image of Ag-TiO$_2$ (1.12 wt.% Ag) nanopowders (a) and its corresponding EDX mapping (b) as well as the EDX maps of elemental distribution for: Ag (c); O (d); Ti (e).

![SEM image](image)

UV–vis diffuse reflectance spectra provide more information regarding the reactions of the photocatalytic materials with photon energy. Fig. 9 shows absorption profiles of Ag-TiO$_2$ composites having different values of silver content compared to pure TiO$_2$.

It was noticed a significant shift of the absorption peak toward the visible regions of the solar spectrum for Ag-TiO$_2$ composite, exhibiting a maximum at around 450–550 nm wavelength and an enlargement of the absorption band (the so-called “tail” of the band), suggesting an increase of the photocatalytic activity within the visible range. An increase of the absorption values in the UV region was also observed for the prepared Ag-TiO$_2$ composites. In addition the absorption intensity increased as Ag concentration is higher. This behavior was usually ascribed to Ag$_x$ nanoparticles inducing visible light absorption [32,33]. Moreover, absorption bands at 400–500 nm may be also attributed to Ag clusters of about 10 nm according to [34,35]. Such shoulder-like peak was usually assigned to the surface plasmon absorption of spatially confined electrons in Ag nanoparticles [32,36].

However, this band presents a quite large displacement as compared to the typical plasmon peak of Ag nanoparticles at 400 nm, which might be related to the potential interaction between silver and TiO$_2$ [33 and included references]. These findings suggest that the applied electrochemical treatment induces a modification of TiO$_2$ structure. This change does not necessarily represent the bulk change inside the oxide, but rather a modification on the surface. Also, the decrease in the energy edge on Ag-TiO$_2$ composites as compared to pure TiO$_2$ may be assigned to the electron acceptor character of the silver nanoparticles [37,38].

3.3. Photocatalytic activity of Ag-TiO$_2$ composites: degradation of Orange II dye solutions

Photocatalytic efficiency depends on the crystalline morphology and the interfacial contact of nanoparticles. Because Orange II compound is an azo dye with a low level of sorption onto powder surface, the suspension solution with the dye was kept in the dark for 30 min (under
continuous stirring) prior to the photocatalysis test. Control experiments were carried out to check the degradation of the dye occurs owing to photocatalysis alone. Thus, blank measurements with the pure Orange II solution under UV illumination (λ = 365 nm) and visible illumination for 3 and 6 h were performed and no significant discoloration of the solution was noticed, confirming that the direct photolysis of the dye is negligible.

The Ag-TiO₂ catalyst concentration in suspension was 0.5 g/L and this concentration was selected to provide a suspension with enough transparency for the UV light assuring enough amount of excited catalyst particles for reliable destruction of the dye. The initial concentration of the dye in all experiments was 20 ppm.

The reaction rate (r) of the heterogeneous photocatalytic degradation (photooxidation) of a dye has been described in several papers by the Langmuir–Hinshelwood mechanism [39,40], which can be expressed by the following equation:

\[
 r = \frac{-dC}{dt} = \frac{k_{ad}C}{1 + K_{ad}C}
\]  
(2)

where C is the dye concentration at a certain time t, k is the reaction rate constant and K_{ad} represents the adsorption coefficient of the dye on the photocatalyst surface.

Fig. 10 presents the decolorization results of 20 ppm Orange II dye solutions in the presence of Ag-TiO₂ composites (having various Ag loadings as compared to pure TiO₂ anatase) for different time intervals during illumination conditions. The percent of residual Orange II at different UV light time intervals decayed as a function of irradiation time, as shown in Fig. 10a. Ag-TiO₂ photocatalysts revealed significantly higher photoactivity than pure TiO₂.

If the dye concentration is low enough, the pseudo-first-order reaction conditions apply and the product K_{ad}C becomes very small as compared to 1 and may be neglected in the denominator of Eq. (2). Integrating Eq. (2) after this simplification leads to the first-order equation (3):

\[
 -\ln \left( \frac{C}{C_0} \right) = k_{ad}t = k_{app}t
\]  
(3)

where \( k_{app} = k_{ad} \) is the apparent pseudo-first-order reaction rate constant and \( C_0 \) is the initial concentration of the dye. Fig. 10 shows the linear relationship of the natural logarithm of the ratio between the concentration of Orange II after

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photocatalytic degradation and its initial concentration versus the corresponding irradiation time. The correlation coefficients ($R^2$) for the fitted straight lines were calculated to be between 0.93 and 0.98 (see Table 2), suggesting that the photocatalytic degradation of Orange II can be described by a first-order kinetic model. The value of $k_{app}$ obtained from the slopes of the linear curves shown in Fig. 10b gives an indication of the activity of the photocatalyst.

As shown in Fig. 10a and b, the photocatalytic degradation of Orange II is enhanced in the presence of Ag-TiO$_2$ composite as compared to pure TiO$_2$. Moreover, the magnitude of Ag content within the composite also affects the photocatalytic rate, in agreement with other literature data [16,38,41,42]. According to our obtained data, Ag-TiO$_2$ composite having 2.71 wt.% Ag content exhibited the highest degradation rate. For this composite, a photodegradation efficiency of 98.5% was determined after 2 h of irradiation, as compared to a value of 87.5% for pure TiO$_2$ after 4 h of irradiation. However, higher Ag loading in composite determined a decrease of the photocatalytic performance, as $k_{app}$ values suggest.

According to the literature [38,41,43], Ag nanoparticles deposited on TiO$_2$ act as electron traps, enhancing the electron–hole separation and the subsequent transfer of the trapped electron to the adsorbed O$_2$ acting as an electron acceptor. Thus, more holes will be able to escape from the geminate hole–electron recombination. It is well known that the geminate recombination is the main reason for low efficiency of TiO$_2$ photocatalysis. Therefore, the existence of silver atom in Ag-TiO$_2$ composite can facilitate more holes to transport toward the surface and enhance the photocatalytic efficiency.

A schematic diagram illustrating the photocatalytic degradation in the presence of Ag-TiO$_2$ composite is presented in Fig. 11.

However, higher silver loadings determine a negative effect. Increasing the Ag content within the composite may result in a photo-hole trapping effect. With the amounts of silver increasing, more catalyst surface area is covered by silver, which prevents TiO$_2$ from contacting with light and this leads to the decrease in yield of photo-induced electron and hole [44].

The assessment of the photocatalytic activity of the electrochemically prepared Ag-TiO$_2$ composites under visible light illumination has been also performed, as illustrated in Fig. 12. Values of 0.0047 for pure TiO$_2$ anatase and of 0.011 min$^{-1}$ for Ag-TiO$_2$ composite containing 2.71 wt.% Ag were obtained for $k_{app}$ under visible light irradiation. These results confirmed the better behavior of the composite as compared to pure TiO$_2$, which has also been detailed in [45].

### 3.4. Antimicrobial activity

#### 3.4.1. Antifungal activity of Ag-TiO$_2$ composite

The antifungal performance of the electrochemically prepared Ag-TiO$_2$ composites has been tested against the fungi mix as was detailed in Section 2.5.1 using: (A) suspension containing 5 g/L Ag-TiO$_2$ (0.8 wt.% Ag) and (B) super concentrated solution (slurry) containing 50 g/L Ag-TiO$_2$ (0.8 wt.% Ag).

Figs. 13 and 14 show examples of photographic images of the inhibition area determined by the presence of Ag-TiO$_2$ composite based solutions on fungi mix growth after various exposure periods. As evidenced in Fig. 13, the presence of (A) suspension containing 5 g/L Ag-TiO$_2$ (0.8 wt.% Ag) inhibited the mold growth around the padded filter paper. The inhibition zone had a diameter of 20–22 mm and it remained unchanged even after 14 days of exposure at the fungi mix action, corresponding to "0" mold index (no mold growth) according to [17].
Fig. 11 – Schematic diagram illustrating the photocatalytic degradation in the presence of Ag-TiO$_2$ composite.

Fig. 12 – (a) Residual Orange II dye after different visible light irradiation times in the presence of pure TiO$_2$ anatase and Ag-TiO$_2$ composite containing 2.71 wt.% Ag; (b) linear plots of ln($C/C_0$) versus the irradiation time.

Fig. 13 – Photographic images of the inhibition zone occurring in the presence of (A) suspension containing Ag-TiO$_2$ composite against the tested fungi mix (see Section 2.5.1) after: (a) 7 days and (b) 14 days of exposure.

The use of more concentrated Ag-TiO$_2$ suspensions, such as (B) solution, facilitated the inhibition of mold growth for extended periods of exposure, as illustrated in Fig. 14. As an example, after 21 days an inhibition zone having a diameter of 20 mm was noticed, corresponding to “0” mold index.

It should be mentioned that additional antifungal assessment tests involving dispersion solutions containing 5 g/L and respectively 50 g/L of pure TiO$_2$ showed a mold index of “3” (≈30% coverage of mold on surface) after 7 days of exposure and of “4” (≈50% coverage of mold on surface), suggesting a very low or even absent fungistatic action. T. viride began to
Fig. 14 – Photographic images of the inhibition zone occurring in the presence of (B) suspension containing Ag-TiO₂ composite against the tested fungi mix (see Section 2.5.1) after: (a) 14 days and (b) 21 days of exposure.

Table 3 – Minimum inhibitory concentration (MIC) values, expressed in μg/mL determined from the quantitative assays of the antimicrobial activity of Ag-TiO₂ composites.

<table>
<thead>
<tr>
<th>Solution type and concentration</th>
<th>MIC, μg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Staphylococcus aureus ATCC 6538</td>
</tr>
<tr>
<td>31.80 ppm Ag*</td>
<td>31.80</td>
</tr>
<tr>
<td>5 g/L TiO₂</td>
<td>R</td>
</tr>
<tr>
<td>5 g/L Ag-TiO₂ (1.4 wt.% Ag)</td>
<td>10.44</td>
</tr>
</tbody>
</table>

R, resistant.

* Data from the previous study [11].

grow after 7 days on the padded filter paper involving the above mentioned solutions based on pure TiO₂.

3.4.2. Antibacterial activity of Ag-TiO₂ composite

The antibacterial effects of the Ag-TiO₂ composites were assessed by determining the minimum concentration needed to inhibit the growth of the test bacterial strains. The obtained minimum inhibitory concentration (MIC) values of the Ag-TiO₂ composite against the tested microorganisms as compared to pure TiO₂ and pure nano-Ag in the form of colloidal solutions are given in Table 3. For pure TiO₂ based colloidal solutions, the inhibition in microorganisms’ growth was not observed.

As shown in Table 3, a concentration of 10.44 μg/mL, which is the highest MIC value is noticed against Gram-positive S. aureus. According to the obtained results, the tested Ag-TiO₂ composite based colloidal solution was most effective against Gram-negative germs (both P. aeruginosa ATCC 9027 and E. coli ATCC 8789).

This tendency is in a good agreement with Zielinska et al. [46] and Yaşa et al. [47] investigations. Based also on experimental results of Kim et al. [48], the antimicrobial effects of Ag-TiO₂ composites may be associated with the characteristics of specific bacterial species. Gram-positive and Gram-negative bacteria have differences in their membrane structure, the most distinctive being the thickness of the peptidoglycan layer.

Additionally, according to the determined values, colloidal Ag-TiO₂ solutions were more effective against the tested bacterial strains at lower concentrations as compared to those corresponding to the colloidal solutions with Ag nanoparticles reported in [11] (that have been electrochemically synthesized using a quasi-similar procedure based on the “sacrificial anode method”), ranging between 10.44 and 6.71 μg/mL of silver.

Overall, the electrochemically prepared Ag-TiO₂ composites as colloidal solutions showed promising antibacterial and antifungal characteristics, so that they may be considered as attractive nanomaterials with potential industrial and medical applications.

4. Conclusions

The performed investigations showed that photocatalytically-active and antimicrobially-active Ag-TiO₂ composites may be successfully synthesized using the so-called “sacificial anode method”, involving a simple experimental set-up. Through a proper selection of the applied current density and electrolysis time, a fine tuning of the silver content within the composite may be obtained, according to the final envisaged application. The proposed electrochemical synthesis procedure is highly efficient and easy to be scaled-up.

The XPS investigations confirmed the presence of Ag on TiO₂ mainly in the metallic state, being consistent with the XRD results, too.

The electrochemically synthesized Ag-TiO₂ composite exhibited in UV–vis diffuse reflectance spectra a maximum at around 450–550 nm wavelength and an enlargement of the absorption band (the so-called “tail” of the band), thus
suggesting an increase of the photocatalytic activity within the visible range as compared to pure TiO₂ anatase.

Photocatalytic activity of the prepared Ag-TiO₂ composites has been determined by photodegradation of Orange II dye solution under UV irradiation (λ = 365 nm). The heterogeneous photocatalytic degradation rate was found to follow a pseudo first order kinetics. According to the obtained data, Ag-TiO₂ composite having 2.71 wt.% Ag exhibited the highest degradation rate constant. Therefore, a photodegradation efficiency of about 98.5% has been determined when Ag-TiO₂ nanopowder was used, as compared to a value of 87.5% in the case of commercial anatase.

In addition, the Ag-TiO₂ composites as dispersion solutions containing 5–50 g/L Ag-TiO₂ (0.8 wt.% Ag) showed good antifungal and antibacterial characteristics. The tested Ag-TiO₂ composite based colloidal solution was most effective against Gram-negative germs (both P. aeruginosa ATCC 9027 and E. coli ATCC 8789), suggesting that the bioactivity depends on the bacterial strain.

These findings are of increasing relevance given the current need for more efficient methods to degrade organic and inorganic pollutants and to control microbial infection. Future work will address the optimization of the nanocomposite formulations suitable to be applied as finishing layers on different solid substrates, including leather, ceramics and metals usually involved in bio-medical applications.

Conflicts of interest

The authors declare no conflicts of interest.

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