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Additional Information

Dyes decolorization using silver nanoparticles supported on nanometric diamond as highly efficient photocatalyst under natural Sunlight irradiation

Premkumar Manickam-Periyaraman¹, Sergio Manuel Espinosa,¹ Juan C. Espinosa,¹ Sergio Navalón,¹ Sivanesan Subramanian,² Mercedes Álvaro,¹ Hermenegildo García^{1,3,*}

¹ Departamento de Química and Instituto de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, Consejo Superior de Investigaciones Científicas, Av. de los Naranjos s/n, 46022 Valencia, Spain

² Department of Applied Science and Technology, Anna University, Sardar Patel road, 600025, Chennai, India

³ Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah, Saudi Arabia

Abstract

Herein we report that silver nanoparticles supported on commercial diamond nanoparticles functionalized with hydroxyl groups (D3) is a cost-effective heterogeneous catalyst for the decolorization of different synthetic dyes (Methylene Blue, Orange II, Acid Red 1 or Rhodamine B) using H₂O₂ as oxidant under natural Sunlight irradiation. Importantly, the photocatalytic activity of Ag/D3 is higher than that of analogous catalysts based on Ag NPs supported on graphite or activated carbon and similar to that of costly Au/D3 catalyst or the benchmark Ag/TiO₂ material. Ag/D3 stability was established by performing consecutive reuses, without observing either

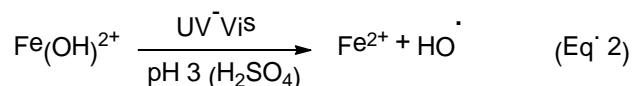
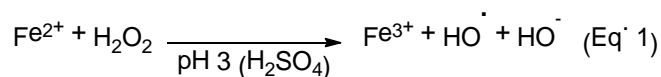
decrease of the catalytic activity or metal leaching, while particle size increase occurs in a low extent. Productivity tests allow determining a minimum TON for dyes and H₂O₂ of about 500 and 6,000, respectively.

Keywords: Photocatalysis; synthetic dyes decolorization; plasmonic Ag nanoparticles; diamond nanoparticles; natural Sunlight irradiation.

1. Introduction

Advanced oxidation processes (AOPs) are among the most useful technologies for the remediation of waste waters containing recalcitrant contaminants or resisting pathogens.[1-3] AOPs are based on the generation of reactive oxygen species such as highly aggressive hydroxyl radicals, superoxide or others, able to oxidize organic contaminants to less-toxic biodegradable intermediates or even to produce their partial or complete mineralization.[1] For example, AOPs have been extensively applied to the treatment of textile waste waters characterized by the production of large volumes of waste water containing colored, toxic and/or mutagenic dyes.[4, 5] It has been estimated that about of 15 % of the produced dyes are released in textile waste waters.[6] Color and chemical oxygen demand (COD) removal represents one major environmental concern in textile waste waters due the inefficacy of conventional biological treatments.[4, 7]

The photo-Fenton reaction is one of the most popular AOPs due its easy implementation and effectiveness in the production of hydroxyl radicals.[8, 9] The reaction proceeds via a redox cycle according to equations 1 and 2 leading to the formation of HO[•] radicals. The main drawbacks the photo-Fenton reaction increasing the operation costs and, therefore, hampering its general application to waste water remediation, are: i) the need of acidic pH values to obtain the correct iron speciation (Eqs 1 and 2) and to avoid iron oxides precipitation; ii) the need of iron removal after the chemical treatment with the subsequent sludge formation; iii) the need of artificial UV irradiation source to promote the photolysis of the Fe(OH)²⁺ complex (Eq. 2) and the existence of undesirable side reactions decreasing the selectivity towards HO[•] formation.



Nowadays, there is an increasing interest on developing heterogeneous photo-Fenton catalysts able to reduce the operating cost as well as to overcome some of the commented drawbacks of the homogeneous process. Currently, the solid-based catalysts employed as heterogeneous photo-Fenton materials include zeolites,[8, 10] clays,[10] pillared clay-based materials,[10, 11] metal oxides,[8] nanosized iron oxides,[12] supported metal[13, 14] or metal oxide nanoparticles[15] and graphenes.[16, 17] Nevertheless, there is still room for improvement basic aspects of the heterogeneous process including minimization of the H₂O₂ excess reducing undesirable decomposition, optimization of H₂O₂ and catalyst to substrate molar ratios, maximization the H₂O₂ to catalyst molar ratio by developing highly efficient (photo)catalysts, expanding the operation pH towards neutral or slightly basic values, use of natural Sunlight irradiation, among others.[8] In this context, we have reported that Au or Ag NPs supported on treated commercial diamond nanoparticles (D) modified by introducing surface hydroxyl groups is an efficient photocatalyst for degradation of phenol as well as its reaction intermediates (hydroquinone, catechol and *p*-benzoquinone) using less than 5.5 equivalents of H₂O₂ under natural Sunlight irradiation[13, 18] Therefore, it is of interest to evaluate the scope of these Fenton catalysts by testing their efficiency in the degradation of other recalcitrant contaminants, particularly decolorization of synthetic dyes that are frequently employed in the textile industry.[10]

In the present work we describe the use of Ag NPs supported on surface hydroxylated D as photocatalyst to effect the decolorization and COD removal of four

common synthetic dyes present in textile waste water effluents namely Methylene Blue (MB), Orange II (OII), Acid Red 1 (AR1) and Rhodamine B using H₂O₂ as oxidant and natural Sunlight irradiation. The activity of this catalyst is compared with analogous Au NPs supported on the same hydroxylated D or Ag NPs supported on nanometric diamond NPs, graphite, activated carbon as well as on the benchmark TiO₂ photocatalyst under natural or simulated sunlight. The purpose is to establish how the pretreatment of the support influences the photocatalytic activity of AgNPs by controlling the average particle size and the surface functional groups. It would be shown that treating the supports under Fenton conditions followed by reduction with H₂ renders the most active supports due to the small particle size and the lower density of surface OH groups. The catalytic data presented compare favorably with those reported in the literature for iron based catalysts that undergo extensive metal leaching and typically operate with H₂O₂ excesses of one thousand equivalents or more. In the case of Ag, the absence of metal leaching and its high activity can make the use of this metal, in low loading, an attractive alternative compared to other metals.[19]

2. Experimental section

2.1 Materials. MB, OII, AR1, RhB, H₂O₂ solution in water (30%, w/w), HNO₃ (65%), NaOH (>97 %) were supplied by Sigma-Aldrich. The other reagents or solvents were of analytical or HPLC grade.

2.2 Catalyst preparation. The catalysts employed in the present work have been previously prepared and fully characterized.[18] The carbonaceous materials employed as support of gold and/or silver NPs include commercial diamond NPs, activated carbon and graphite. The commercial carbon supports were also functionalized by a homogeneous Fenton treatment followed or not by a hydrogen annealing at 500 °C and

further employed to deposit gold or silver NPs. Ag NPs supported on commercial TiO₂-P25 was also employed as benchmark photocatalyst.[18] Fig S1 presents the full set of FTIR spectra for each of the samples used as support.

2.3 Catalyst characterization. The five-time used Ag/D3 catalyst was characterized using a JEOL JEM2100F transmission electron microscope operating at 200 kW. The silver particle size distribution of Ag/D3 was estimated by counting more than 300 particles working under dark-field scanning transmission electron microscopy (DF-STEM) mode. The silver leaching was determined by ICP-AES of filtered reaction aliquots (0.2 μm Nylon) at the end of the reaction. The reader has referred to previous work for XRD, DRS textural data and further characterization of Ag/D3.[18]

2.4 Photocatalytic experiments. The photocatalytic experiments were carried out at least in triplicate (March-July, 2015, Technical University of Valencia, Valencia, Spain). A round-bottom flask (250 mL) containing an aqueous dye solution (25 mL; 0.071 mM) and the required amount of catalyst (typically 80 mg L⁻¹ unless other quantity indicated) was added sonicated for at least 20 min. The large flask volume in comparison with the volume of the sample ensures as high degree of aeration of the dye solution and large surface exposure to sunlight. Then, the initial pH value of the aqueous suspension was adjusted to the required value using aqueous solutions of HNO₃ (0.1 M) or NaOH (0.1 M). The samples were exposed for five minutes to natural Sunlight irradiation before adding H₂O₂ until the temperature was equilibrated. The reaction starts by adding the required amount of H₂O₂. In all cases, to minimize the metal leaching from the solid catalyst to the solution, the pH of the reaction was not allowed to become lower than 4, checking, and readjusting the pH if, necessary, every fifteen minutes with a pH meter CRISON 52 02 pH electrode, using aqueous solutions

of HNO₃ (0.1 M) or NaOH (0.1 M). The natural Sunlight irradiation intensity was measured using a calibrated photodiode connected to a voltmeter. During the experiments performed in the present work the mean solar irradiation and temperature were $86 \pm 17 \text{ mW cm}^{-2}$ and $26 \pm 2.2 \text{ }^\circ\text{C}$, respectively. To diminish the influence of the unavoidable variation of solar light irradiance from different days, the experiments were carried out in sets of simultaneous photocatalytic tests carried out in parallel. These sets correspond to the influence of the support for AgNPs (Fig. 1), the influence of the nature of the metal (Ag or Au, Fig. 2), comparison of the catalytic activity of Ag on D3 or TiO₂ in the presence or absence of H₂O₂ (Fig. 3). The temporal evolution of the reaction was monitored by taking periodically aliquots (2 mL) that were diluted to a final volume of 10 mL. In one experiment (Figure S2) reaction aliquots of 0.5 mL were taken and diluted to a final volume of 5 mL. These diluted samples were split into two to determine for each of them the dye concentration and the H₂O₂ consumption.

Reuse experiments were performed following the general procedure and filtering the solid catalyst at the end of the reaction (0.2 μm nylon membrane). Then, the recovered catalyst was washed with a basic aqueous solution (pH 10) and then with Milli-Q water to remove possible adsorbed acid organic compounds. Then, a new photocatalytic reaction using the recovered catalyst was carried out. To avoid possible irradiation variations during the reuse experiments and productivity test they were not performed under natural Sunlight irradiations. Instead natural Sunlight, a solar simulator (Oriel Sol1A) was employed in this case as irradiation source working with a light intensity of 100 mW cm^{-2} (1 Sun) at $20 \text{ }^\circ\text{C}$.

Productivity tests were performed using a large amount of dye (0.71 mM) and H₂O₂ (7.1 or 10.6 mM) respect to the catalyst (80 mg L⁻¹; 0.00149 mM of supported Ag) at pH 4.

2.5 Analysis of dye concentration and H₂O₂. Dye concentration was determined by measuring the UV-Vis spectra of previously filtered reaction aliquots in a JASCO-650 spectrophotometer. In order to maintain the linear relationship of the Lamber-Beer law the samples were diluted using Milli-Q water. Dye concentration was determined using a linear calibration plot previously obtained using standards with known concentration. Degradation of the dyes is presented by plotting dye concentration as a function of the illumination time.

H₂O₂ concentration was also determined using the UV-Vis spectrophotometer following a colorimetric method.[18] Briefly, diluted samples were titrated using a solution of K₂(TiO)(C₂O₄)₂ in H₂SO₄/HNO₃ and after 10 min the developed yellow color monitored at 400 nm. It should be noted that strong acidic conditions needed for determination of H₂O₂ concentration by colorimetric method result in a complete decolorization of the dyes, thus allowing selective monitoring of TiO- H₂O₂ adduct by determining absorbance at 400 nm without interference of any of the dyes under study.

2.6 COD measurements. COD values were determined by a closed reflux method following the procedure described in detail in the Standard Method Nr. 5220D.[20]

2.7 Toxicity tests. A Microtox® M500 toxicity analyzer was employed to measure the chemical toxicity against the bioluminescent photobacterium *Vibrio Fisheri*. [21] The toxicity units (T.U.) are defined as 100/EC₅₀, where EC₅₀ is the percentage of solution

that causes 50 % inactivation. This inactivation is measured as the reduction of the 50 % light emission by *Vibrio Fischeri* after 50 min contact time.

3. Results and discussion

3.1 Photocatalysts tested

The present work includes the use of eleven photocatalysts based on Au or Ag NPs supported on different carbonaceous supports as well as on TiO₂-P25 as benchmark photocatalyst (Table 1 and S1). In the case of Ag NPs supported on TiO₂, the catalytic activity of Ag promoting generation of OH· from H₂O₂ would be combined with the well-known photocatalytic activity of semiconducting TiO₂ generating ROS. In contrast to the activity of TiO₂, the other solid supports do not exhibit any photocatalytic activity, either in the absence or presence of H₂O₂. This lack of photocatalytic activity for D and other supports ruled out the possible metal impurities that could be present in the ppm levels such as Fe could contribute in an extent to the photocatalytic activity of observed support Ag NPs. The carbonaceous supports include the commercial D NPs (D1), commercial graphite (G1) and commercial activated carbon (AC1). In addition, each commercial carbonaceous support was also submitted to a homogeneous Fenton treatment to remove amorphous carbon impurities and to increase the population of oxygenated functional groups on the carbon surface, mainly hydroxyl, carbonylic and carboxylic groups. The Fenton-treated carbonaceous materials were denoted as D2, G2 and AC2 for D, graphite and active carbon, respectively. In a second step, the Fenton-treated materials were submitted to H₂ annealing at 500 °C in order to homogenize the distribution of surface oxygenated functional groups carbonaceous surface with hydroxyl functional groups. The resulting supports were denoted as D3, G3 and AC3 for D, graphite and active carbon, respectively. Fig. S1 in Supporting Information

presents the FTIR spectra corresponding to the three types of carbon support (D, G and AC) after the corresponding pretreatment. As it can be seen there, the population of hydroxyl groups clearly increases for each support after the Fenton treatment (D2, G2 and AC2) and, then, is maintained (G3) or decreases somewhat (D3 and AC3) in the thermal hydrogen annealing. Finally, Au or Ag NPs were deposited in the different carbonaceous supports or TiO₂-P25 by means of the polyol method that employs ethylene glycol as reducing agent of the corresponding metal salt precursors of Au or Ag NPs namely HAuCl₄ or AgNO₃. In previous work full characterization of the photocatalysts including both the support materials as well as the deposited metal NPs has been reported.[18, 22, 23] It is important to note that the smallest metallic NPs deposited on the different carbonaceous supports were observed when using the Fenton-treated carbonaceous material followed by a H₂ annealing at high temperature (Table 1 and S1). For comparison, Ag/TiO₂ as a benchmark photocatalyst was also included in the present work (Table 1, entry 6).[18]

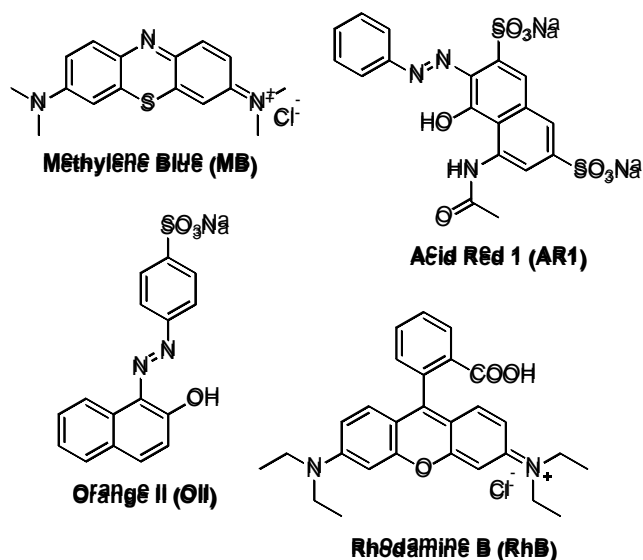
Table 1. List of the most active catalysts employed in the present work.^a

Entry	Catalyst	Surface area and average particle size of the support	Average particle size (nm) and standard deviation of deposited metallic NPs	Initial reaction rate of H ₂ O ₂ decomposition	Ref.
1	Au/D3	~ 290 m ² g ⁻¹ < 10 nm	2.9 ± 3.6	0.33 mg·L ⁻¹ ·min ⁻¹	[18]
2	Ag/D3	~ 290 m ² g ⁻¹ < 10 nm	3.2 ± 2.7	0.27 mg·L ⁻¹ ·min ⁻¹	[18]
3	Ag/D3 five-times reused	~ 290 m ² g ⁻¹ < 10 nm	3.6 ± 3.3	0.17 mg·L ⁻¹ ·min ⁻¹	This work
4	Ag/G3	47 m ² g ⁻¹ , 200-500 nm	8.5 ± 4.4	0.04 mg·L ⁻¹ ·min ⁻¹	[18]
5	Ag/AC3	1,300 m ² g ⁻¹ , 149 µm	8.9 ± 7.6	0.1 mg·L ⁻¹ ·min ⁻¹	[18]
6	Ag/TiO ₂	~ 50 m ² g ⁻¹ , ~ 25 nm	3.1 ± 1.6	0.53 mg·L ⁻¹ ·min ⁻¹	[18]

^a Supplementary material collects a list of the rest of the catalysts employed in the present work including data on Ag NPs average particle size and standard deviation.

3.2 Photocatalytic dye decolorization

In the present work the photocatalytic activity of different Ag or Au materials supported on D-, G-, AC- or TiO₂ based catalysts has been tested for the decolorization of MB, OII, AR1 and/or RhB at submillimolar concentrations, that is in the range in which these dyes can be frequently present in wastewaters from the textile industry (Fig. 1). Four of the most common dyes present in textile waste waters have been selected (see chemical structures in Scheme 1) including a thiazine dye such as MB, two azo dyes (OR II and AR1) and RhB as aminoxanthene dye.[10, 24]



Scheme 1. Chemical structures of the dyes employed in the present work.

To better show the activity of the different photocatalyst under study, the use of natural sunlight as irradiation source was selected for most of the experiments shown in Fig. 1-3. Only for reuses and productivity test that cannot be run simultaneously in parallel were performed using simulated sunlight. When using natural sunlight, variations in light irradiance are unavoidable (see Experimental Section for sunlight intensity variation). To minimize this influence, the experiments were performed in sets simultaneously and the sets correspond to the experiments collected in the same figures.

Firstly, the light-assisted catalytic activity of Ag NPs supported on commercial carbonaceous supports (D1, G1 and AC1), on Fenton-treated carbonaceous supports (D2, G2 and AC2) as well as on Fenton-treated and subsequent H₂ annealed supports (D3, G3 and AC3) was compared for MB decolorization with H₂O₂ under natural Sunlight irradiation at pH 4 (Figs. S2 to S4). The highest photocatalytic activity was observed when using Ag NPs supported on the carbonaceous material (D3, G3 or AC3) modified with a homogeneous Fenton treatment followed by H₂ annealing at high temperature (Fig. 1 and S2-S4). Note that in Figs. 1 and S4 the behavior of G3 and AC1

as support, respectively, corresponds really to adsorption since the decrease in MB concentration occurs exclusively after contacting MB and the photocatalyst in the first minutes and it is not accompanied by a concomitant decrease in the H₂O₂ concentration. This lack of photocatalytic activity of Ag/AC1 (Fig. S4) or low activity for Ag/G3 (Fig. 1) allow to determine that the dye adsorption in these cases is very important and corresponds to about 80 (Ag/AC1) or 20% (Ag/G3) of the initial MB concentration. However for Ag/AC2, the importance of adsorption is reduced about 60% and for Ag/AC3 adsorption corresponds to 40% of the initial dye concentration. This superior catalytic activity of Fenton-treated support can be quantitatively assessed by the initial reaction rate of H₂O₂ decomposition that would correspond to the maximum amount of generated active species over the different photocatalysts. Table 1 lists these initial reaction rates for the most active photocatalysts. The order of catalyst activity can be rationalized as derived from the smaller particle size distribution of Ag NPs supported on D3, AC3 or G3 solids respect to the use of commercial (D, AC or G) or Fenton-treated samples (D2, AC2 or G2) supports (Table 1 and S1) and also to the surface modification of the support. Fenton treatment should remove from the surface those surface groups that could later react with hydroxyl radicals during the light assisted Fenton decolorization of the dyes. Previous characterization has shown that in the case of D, the pretreatments used in the preparation of D3 removes oxygenated functional groups, particularly carboxylic acids and carbonyls from the surface. Fig. 1 also shows that Ag/D3 exhibits remarkable higher photocatalytic activity respect to the use of Ag/AC3 or Ag/G3 again attributed to the smallest Ag NPs supported in the former catalyst and the inertness of diamond surface respect to other supports. It should be noted that this behavior, i.e. higher catalytic activity for the smallest supported metal

NPs, has been frequently observed when using MNPs deposited on heterogeneous supports.[22, 23, 25]

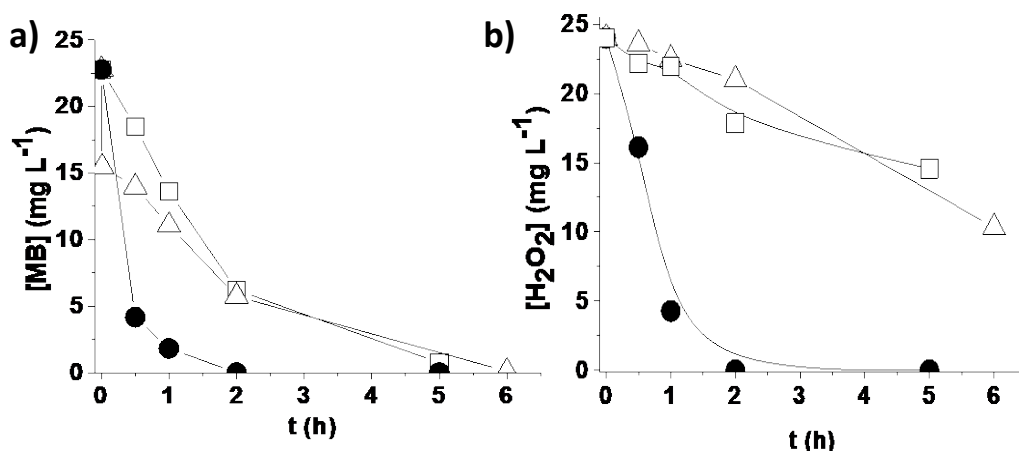


Fig. 1.

Importantly, Ag NPs supported on D3 behave similarly than an analogous Au/D3 catalyst for MB decolorization with H₂O₂ under natural Sunlight irradiation. This observation is a clear example of the possibility to replace expensive noble metals such as Au by others more cost-effective ones, such as Ag, while maintaining the catalytic activity (Fig. 2). Furthermore, the beneficial influence of irradiation of Ag NPs by natural Sunlight can be observed respect twin experiments carried out in the dark. The effect of light can be attributed to the photoejection of electrons from excited Ag NPs generated by irradiation with wavelengths coincident with the surface plasmon band absorption (SPB) of Ag NPs.[18, 26] A blank control experiment where MB with H₂O₂ was exposed to natural Sunlight irradiation in the absence of catalyst shows also some MB decolorization, but requiring much longer reaction times. This fact is not unexpected since dyes such as MB are well-known photosensitizers that can promote the formation of reactive oxygen species such as singlet oxygen able to cause self-degradation of the dye.[27] Nevertheless, as it will be commented later in the

productivity tests, the use of higher dye concentrations ($> 250 \text{ mg L}^{-1}$) clearly shows the beneficial use of Ag/D3 with H_2O_2 under natural Sunlight irradiation not only in the case of MB, but also in when using OII, AR or RhB.

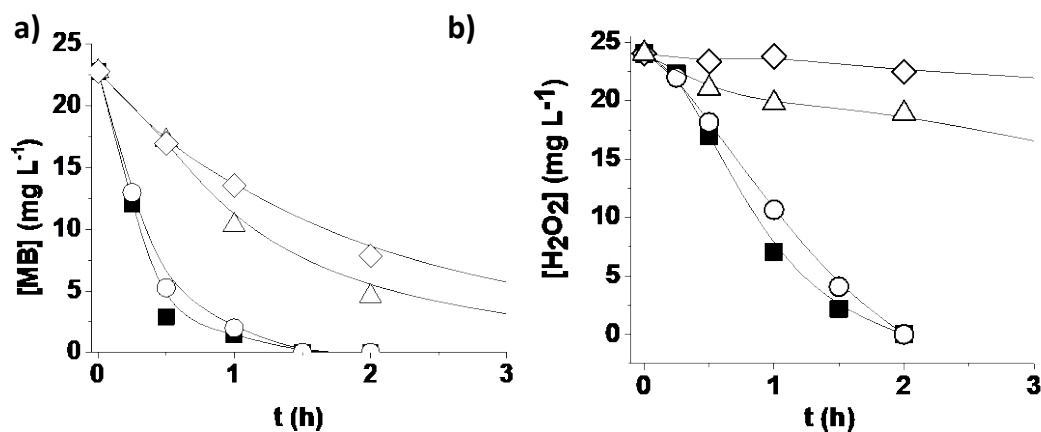


Fig. 2.

The photocatalytic activity of Ag/D3 with H_2O_2 was also compared to that of the benchmark photocatalyst Ag/TiO₂ for the degradation of different dyes such as MB, AR1, OII and RhB under natural Sunlight irradiation (Figs. 3 and S5). A well established fact is that TiO₂ lacks photocatalytic activity upon visible light irradiation due to its large band gap and also that the presence of metal nanoparticles is required to increase the photocatalytic activity of TiO₂. In general, the results indicate that Ag/D3 compares favorably in terms of fast dye decolorization to the use of Ag/TiO₂ without H_2O_2 (compare Ag/TiO₂ with (○) and without H_2O_2 (▲)). It seems that Ag/TiO₂ either in the presence or absence of H_2O_2 under aerated conditions in water generate hydroxyl radicals, the difference according to Fig. 3a (compare Ag/TiO₂ with (○) and without H_2O_2 (▲)). Then the flux of hydroxyl radicals that is much higher when H_2O_2 is present in the aqueous phase and similar or better respect to the use of Ag/TiO₂ with H_2O_2 . Related to these results a previous work has shown that Ag/D3 is more effective than Ag/TiO₂ for the degradation of phenol and its reaction intermediates due to the higher

efficiency of the former to decompose H_2O_2 to HO^\cdot radicals.[18] All together makes Ag/D3 a reasonable alternative photocatalyst for the degradation of pollutants in water using H_2O_2 as oxidant under natural Sunlight irradiation.

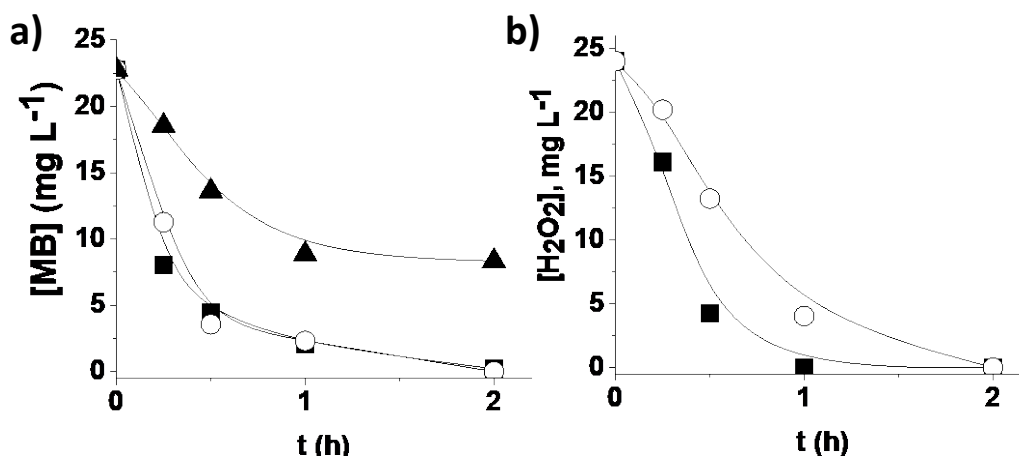
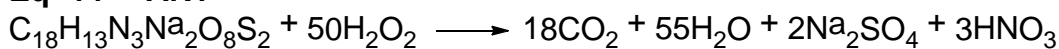
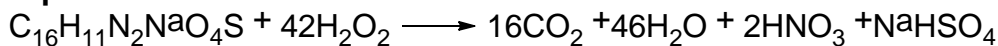
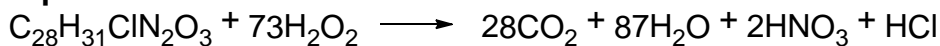


Fig. 3.

One important point of the photo-Fenton process is the optimization of the H_2O_2 amount and, therefore, reducing the operational cost of the process.[28-30] In fact, it is well-established that an excess of H_2O_2 can be detrimental in the process due to the spurious H_2O_2 decomposition to O_2 caused by H_2O_2 quenching of the HO^\cdot radicals.[29] For this reason is important to test the efficiency of novel heterogeneous (photo)Fenton catalysts in terms of consumed H_2O_2 versus substrate degradation. To address this point we have considered the theoretical H_2O_2 stoichiometry for complete dye mineralization a reference value (Eqs. 3-6). Nevertheless, it should be considered that the amount of H_2O_2 should be minimized as much as possible and complete mineralization of the pollutant using an excess of H_2O_2 is far from being a realistic target due to its low economic viability. A more realistic aim of AOP is to achieve decolorization, reducing the toxicity of the waste water and maximizing COD removal.

Eq'3 for MB**Eq' 4 for AR1****Eq' 5 for OII****Eq' 6 for RhB**

In our study, Figs. 4 and S6 show that MB decolorization can be achieved using just 10 equivalents of H_2O_2 respect to the dye. Decolorization of the dye (band centered at 650 nm) occurs by cleavage of conjugated double bonds, accompanied by dearomatization (band centered at 280 nm), due to the fact that color is mainly due to the existence of conjugated C=C or N=N bonds present in the aromatic dye structure.[31] Similar conclusions can be drawn for AR, OII or RhB for which a minimum H_2O_2 to dye molar ratio of 10, 10 and 15, respectively, is needed for the decolorization/dearomatization process (Figs. S7-S11). To put the present results into context it should be mentioned that related precedents employ a much higher H_2O_2 to dye molar ratio to achieve similar decolorization as in the present study. For example, using heterogeneous photo-Fenton catalysts such as magnetic porous carbon microspheres a H_2O_2 to MB molar ratio of 32 was used.[32] In the case of vanadium-doped iron oxides a H_2O_2 to MB molar ratio as high as 3,000 was employed.[33] In the present work the low H_2O_2 to dye molar ratio needed for the decolorization and dearomatization of the different dyes tested (MB, OII, AR and RhB) reveals the efficiency of Ag/D3 for H_2O_2 decomposition into reactive oxygen species (ROS) such as HO^\cdot radicals.[18]

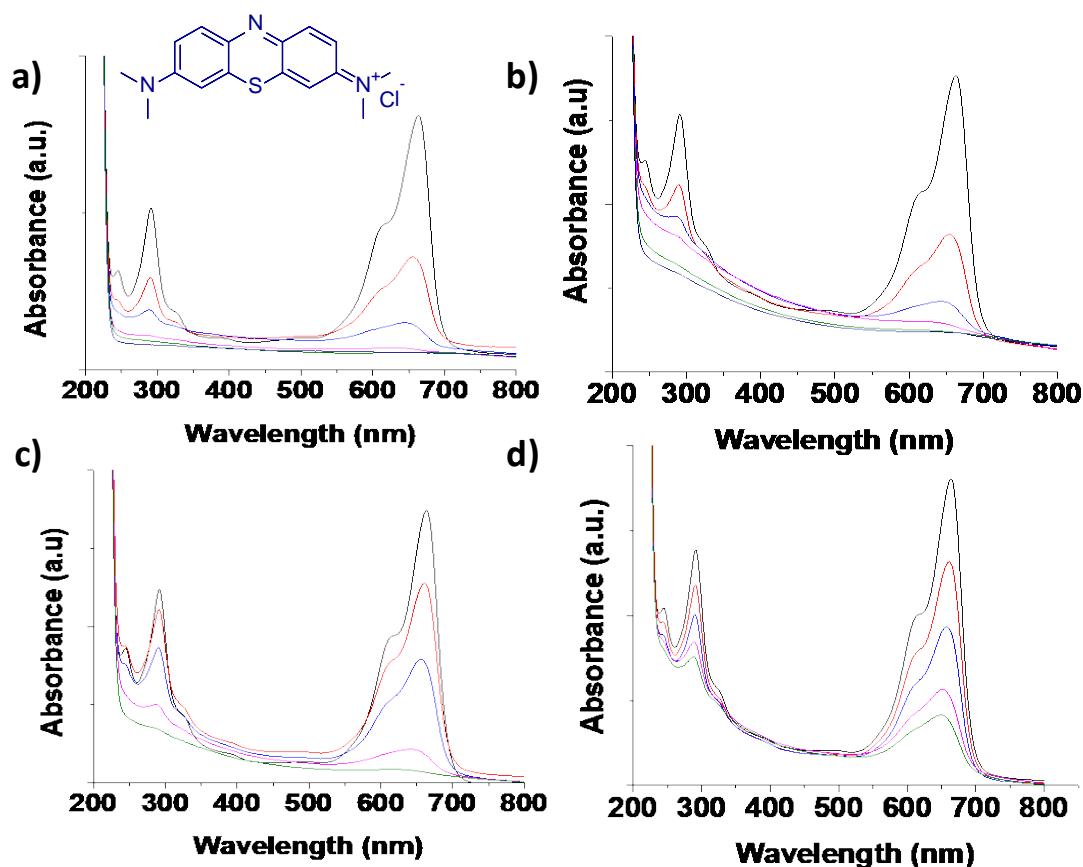


Fig. 4.

As commented before, an important parameter to be considered when optimizing the H_2O_2 to dye molar ratio needed in the AOP is the toxicity of the resulting treated water. There are in the literature some studies showing that regardless the efficiency of some AOPs such as O_3/H_2O_2 , UV/H_2O_2 for the degradation of organic contaminants present in waste waters, the treated water becomes even more toxic than the untreated one.[13, 34, 35] This fact is mainly due to the formation of small aromatic compounds with recognized toxic character such as phenols or aromatic amines.[13, 36] One of the most widely used methods to evaluate the toxicity of aquatic systems is that based on the *Vibrio Fisheri* toxicity test.[37] This test consists in the measurement of the bioluminescence inhibition due to the presence of toxic contaminants in water. With these precedents in mind we tested the toxicity to the *Vibrio Fisheri* bacteria of the MB

solution at pH 4 before and after the heterogeneous (photo)Fenton treatment using Ag/D3 as catalyst with the optimized 10 equivalents of H₂O₂ respect to the dye under natural Sunlight irradiation. Importantly, the initial toxicity of the MB solution (67 T.U.) is completely removed after the treatment (< 3 T.U.) where H₂O₂ has been consumed with the subsequent dye removal (absence of significant absorption at 650 nm) as well as dearomatization of the system (based on the absorption of the 280 and 240 nm peaks). In addition to the toxicity removal, the optimized H₂O₂ dose allowed the COD reduction for each dye from around 1,470 mg L⁻¹ to less than 100 mg L⁻¹ O₂ (Table S2). The resulting COD values being below the limit (125 mg L⁻¹ O₂) established by European regulations for treated waste waters.[38]

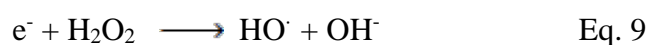
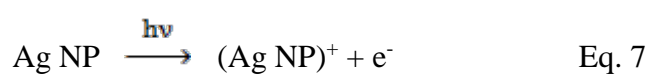
One of the most limiting factors to apply the homogeneous (photo)Fenton reaction is the need to work under acidic conditions (pH 3).[39] This requirement needed to maximize the presence of the photoactive Fe(OH)²⁺ that under UV-Vis irradiation generates HO· radicals and, also, to avoid iron precipitation and minimize the presence of HOO· peroxide anion. In this regard developing heterogeneous (photo)Fenton catalysts able to work at quasi neutral or slightly basic pH values is an important goal.[28-30] In this work, we evaluate the photocatalytic dye decoloration using Ag/D3 as catalyst under natural Sunlight irradiation as a function of the initial pH value of unbuffered aqueous solution (Figs. S13-S16). In general, the photocatalytic activity of AgD3 increases as the pH decreases, but still efficient photo-Fenton decolorization can be achieved at pH 5. This pH value, although still acidic, is significantly higher than the one required for homogeneous photo-Fenton promoted by Fe³⁺ that requires a pH value of three. As commented before, in the absence of catalyst

there is also dye decolorization attributed to the occurrence of light absorption by the dyes promoting their self-degradation in the presence of H₂O₂ as a function of the pH.

To gain some insight about the effect of the pH in the decolorization process in the presence of catalyst under natural Sunlight irradiation, selective radical quenching experiments were performed. In particular, we studied the effect of the presence of DMSO, a very well-known hydroxyl radical scavenger,[13, 18] in the MB decolorization with H₂O₂ under natural Sunlight irradiation as a function of the initial pH value. Fig. S17 shows that the inhibition of MB decolorization in the presence of DMSO in the reaction mixture decreases as the pH increases. This fact is interpreted considering that HO· radicals are the main radicals species responsible of MB decoloration at pH values around 4, while as the pH increases other ROS presumably HOO· or superoxides are involved in the decolorization process.[40] In a previous study on Fenton degradation of phenol by an analogous D supported Ag catalyst, generation of HO· radicals was unambiguously confirmed by trapping with PBN and EPR detection of the corresponding adduct. In contrast, similar study but in the absence of catalyst reveal that the main ROS may be others than HO· radicals such as HOO· radicals or singlet oxygen (Fig. S18).

Based on the well known influence of the pH on the photo-Fenton generation of the HO· radicals and the well known use of DMSO as HO· radicals quencher, the results shown in Figures S17 and S18 provide experimental support to the occurrence of a photo-Fenton process at pH values of 4 and 5 while peroxidation prevails at pH 7.5. In the absence of photocatalyst (Fig. S18), no photo-Fenton occurs. Equations 7 to 9 summarize the photo-Fenton reaction taking place in the presence of AgNP photocatalyst at acid pH values. According to this mechanism the support have to play

at least two main roles, controlling the average AgNP particle size to ensure the operation of the electron confinement responsible for Plasmon band that should absorb photons and eject electrons and also to be sufficiently inert to allow HO[•] radicals to migrate freely to the aqueous phase as free radicals without becoming attached to the surface. As it can be seen in Table 1 Ag/D3 combines a small average Ag particle size (3.6 nm) together with an inert support since D3 have been already submitted to Fenton treatment.



Finally, the stability of the Ag/D3 was assessed by performing reuse and productivity experiments. Fig. 5 shows that Ag/D3 catalyst can be employed for at least five consecutive times without observing decrease of the photocatalytic activity and without observing significant silver leaching from the solid catalyst to the solution (<0.5 wt % of the initial supported silver) as revealed by ICP-OES measurements. Furthermore, TEM analysis of the five-times used Ag/D3 sample shows that the silver particle size has been maintained (Fig. S19). Thus, the absence of silver leaching and the absence of Ag NPs aggregation are the main factors responsible of the good catalytic activity of Ag/D3 upon reuse for MB decolorization using H₂O₂ as oxidant under simulated Sunlight irradiation. The relatively minor decay in catalytic activity observed could be attributed to partial Ag NP oxidation and corresponding passivation of the external surface of the metal NPs.

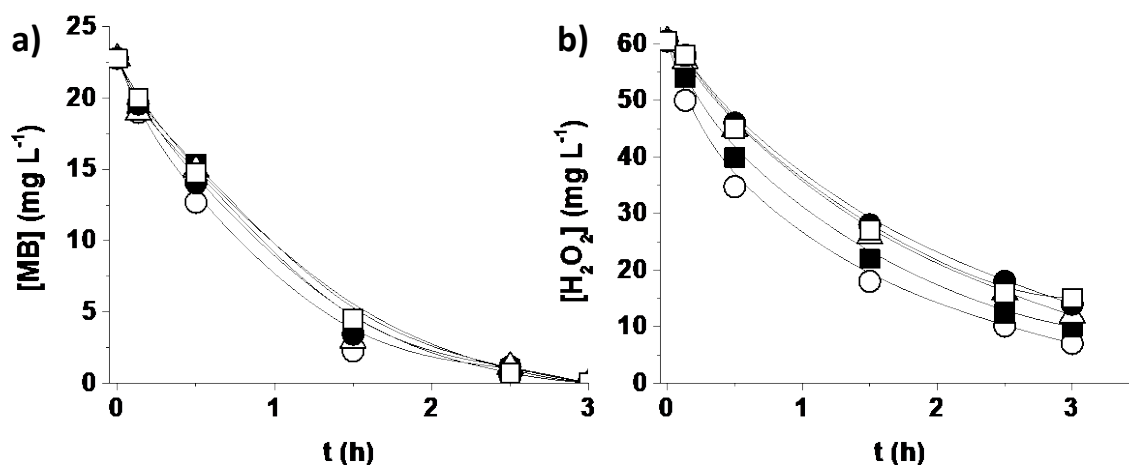


Fig. 5.

Productivity tests using concentrated dye solutions ($250\text{-}300 \text{ mg L}^{-1}$, 0.71 mM) with a minimum catalyst concentration (80 mg L^{-1} , 0.00149 mM as Ag) indicate the ability of the catalyst to perform a large number of catalytic cycles (TON_{dye} 476 and $\text{TON}_{\text{H}_2\text{O}_2}$ about 6,000) without significant loss of catalytic activity (Fig. 6). Blank control experiments were carried out in the absence of catalyst or in the absence of natural Sunlight (Fig. S20) and show low catalytic activity compared to those experiments in which catalyst was present and the suspension was irradiated with natural Sunlight. These experiments show again the beneficial effects of SPB irradiation of Ag/D3 under natural Sunlight irradiation as photocatalyst for dye degradation by H_2O_2 .

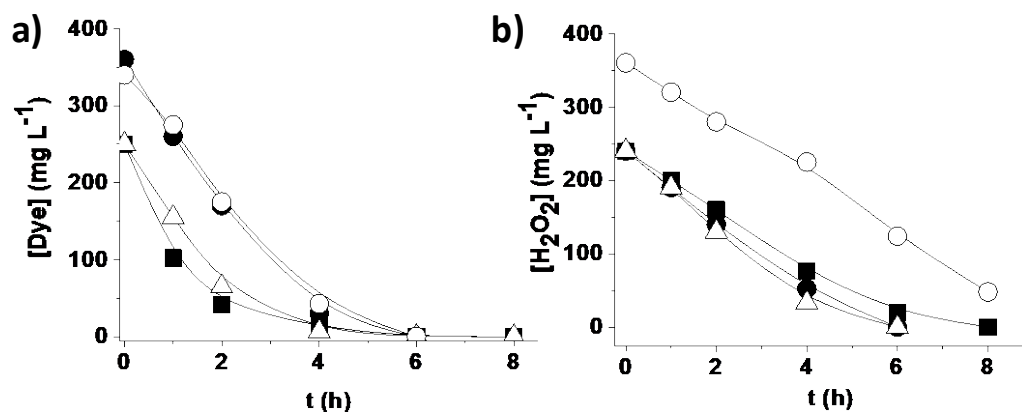


Fig. 6.

Conclusions

In the present work we have demonstrated that Ag NPs supported on commercial D NPs previously functionalized by a homogeneous Fenton treatment followed by H₂ annealing at high temperature is an efficient photo-Fenton catalyst to promote the decolorization of different dyes including MB, OII, AR and RhB under natural Sunlight irradiation with minimal H₂O₂ consumption and achieving remarkable detoxification levels. Ag/D3 as photocatalyst can be reused without undergoing metal leaching and with minimal Ag NPs aggregation. Maximum TON values for dyes and H₂O₂ of about 476 and 6,000 respectively were obtained. Overall this activity data compare favorably those reported in the literature for iron based catalyst that undergo extensive metal leaching and require a large excess of H₂O₂.

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Figure captions

Fig. 1: MB decolorization (a) and H₂O₂ decomposition using Ag NPs supported on D3(●), G3(Δ) and AC3(□) as photocatalysts under natural Sunlight irradiation. Reaction conditions: Catalyst (80 mg L⁻¹, 0.0037 mM of supported Ag), dye (23 mg L⁻¹, 0.071 mM), H₂O₂ (24 mg L⁻¹, 0.71 mM), pH 4.

Fig. 2: MB decolorization (a) and H₂O₂ decomposition (b) using Au (■) or Ag (○) NPs supported on D3 under natural Sunlight irradiation. Blank control under same reaction conditions but in the dark using Ag/D3 (Δ) or in the absence of catalyst (◇). Reaction conditions: Catalyst (0.00149 mM of supported Ag or Au), dye (23 mg L⁻¹, 0.071 mM), H₂O₂ (24 mg L⁻¹, 0.71 mM), pH 4.

Fig. 3: MB decolorization (a) and H₂O₂ decomposition (b) using Ag/D3 (■) or Ag/TiO₂ with (○) and without H₂O₂ (▲). Reaction conditions: Catalyst (80 mg L⁻¹, 0.00149 mM of supported Ag), dye (23 mg L⁻¹, 0.071 mM), H₂O₂ (24 mg L⁻¹, 0.71 mM), pH 4.

Fig. 4: Variation of the UV-Vis absorption spectrum of MB as a function of the amount of H₂O₂ on MB decolorization using Ag/D3 as catalyst. Legend: H₂O₂ to MB molar ratio 20 (a), 10 (b), 5 (c) and 2.5 (d). Reaction conditions: Catalyst (80 mg L⁻¹, 0.00149 mM of supported Ag), dye (23 mg L⁻¹, 0.071 mM), H₂O₂ (as indicated in the legend), pH 4, reaction time 2 h.

Fig. 5: Reusability experiments for MB decolorization (a) and H₂O₂ decomposition (b) using Ag/D3 catalyst under simulated Sunlight irradiation. Legend: 1st use (○), 2nd use (■), 3th use (□), 4th use (●). Reaction conditions: Catalyst (80 mg L⁻¹,

0.00149 mM), dye (23 mg L⁻¹, 0.071 mM), H₂O₂ (24 mg L⁻¹, 0.71 mM), pH 4 and simulated Sunlight irradiation (1 Sun).

Fig. 6: Productivity tests for decolorization of each of the four dyes (a) and the corresponding H₂O₂ decomposition (b) using AgD3 as catalyst under natural Sunlight irradiation. Legend: MB (■), OII (Δ), AR (●) and RhB (○). Reaction conditions: Catalyst (80 mg L⁻¹, 0.00149 mM of supported Ag), dye (0.71 mM), pH 4, H₂O₂ (7.1 mM for MB, OII and AR1; 10.6 Mm for RhB).

