Degradation of the O-phenylphenol Fungicide in Water by Unconventional CeO$_2$-WO$_3$ Photocatalysts

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Abstract: Background: Water pollution due to emerging contaminants such as pesticides, pharmaceuticals and/or plasticizers, is a serious environmental problem strictly connected to the safety of human and ecosystem life. For this reason, the development of high-performing (photo)catalysts for water purification is crucial.

Objective: In recent years, the synergistic effects in Advanced Oxidation Processes (AOPs) can perform better strategies to remove recalcitrant contaminants from water. In this context, the (photo)catalytic activity of CeO$_2$-WO$_3$ materials for the degradation of the ortho-phenylphenol fungicide comparing the photocatalytic, the Fenton and the photo-Fenton-like processes, has been examined.

Methods: The samples were synthetized through deposition-precipitation mediated with the hexamethylenetramine (HMTA) surfactant. The chemico-physical properties of the materials were examined by Raman, UV-Vis Diffuse Reflectance (UV-vis DRS) and X-Ray photoelectron (XPS) spectroscopies. N$_2$ adsorption-desorption measurements and transmission electron microscopy (TEM). The (photo)catalytic measurements were made through a home-made photoreactor irradiated by a solar lamp. The degradation of the fungicide was measured by UV-vis spectroscopy.

Results: An efficient heterojunction was formed between the CeO$_2$ and the WO$_3$ oxides, which provided a good degradation percentage of the pesticide (65%) employing the solar photo-Fenton-like reaction that was the best performing process among the three investigated AOPs. The addition of WO$_3$ on CeO$_2$ facilitated the ionic exchange between the Ce and the W ions, boosting the redox properties of cerium oxide.

Conclusion: The strong interaction between CeO$_2$ and WO$_3$ and the peculiar properties of this unconventional composite pave the way to its use as a promising material for water depollution.

Keywords: AOP, photocatalysis, photo-fenton, pesticides, water purification, CeO$_2$, WO$_3$.

1. INTRODUCTION

Water purification is fundamental for wildlife, human health and the environment. Worldwide, water pollution by chemicals, nutrients, metals, and recently by emergent contaminants as pesticides and pharmaceuticals is increasing [1, 2]. In particular, the agro-industry strongly affects the aquatic ecosystems, due to the large consumption of organic substances (pesticides and fertilizers) and the demand for a high quantity of water [3].

Furthermore, these organic compounds, also at low concentrations, are recalcitrant to the conventional wastewater processes [4].

For these reasons, the development of new green technologies, possibly combined with the widely used water treatment processes, can be a solution to efficiently degrade these persistent pollutants.

In the last years, the Advanced Oxidation Processes (AOPs) were applied to eliminate these kinds of contaminants. These processes involve the formation of highly reactive oxidizing species as superoxide and the hydroxyl radicals, which in turn can degrade the emerging water contaminants as pesticides [5, 6].

In particular, photocatalysis with TiO$_2$ is a widely used and performing AOP that combines milder and green conditions compared to the standard oxidation routes, also ensuring good performance. For these reasons, it is increasingly applied for wastewater treatments [7-9].
The Fenton and the photo-Fenton processes are other valuable examples of techniques able to remove the emerging pollutants.

The first one involves the formation of hydroxyl radicals through the reduction of the \( \text{H}_2\text{O}_2 \) and the oxidation of \( \text{Fe}^{2+} \) ions to \( \text{Fe}^{3+} \) [10]. The process can be improved by the application of a visible or near-ultraviolet irradiation which boosts up the regeneration of the ferrous ions with further production of OH radicals (photo-Fenton process) [11].

The easiness of these AOPs that require inexpensive materials (Fe-based salts) allowed their use alone or in combination with other water treatment technologies [12, 13]. Another fascinating method to further enhance the degradation efficiency of these processes, especially with the recalcitrant contaminants, is the exploitation of the synergistic effects of two or more AOPs [14-16]. This requires versatile catalysts that can be used in a multi catalytic approach. In this context, the cerium oxide (CeO\(_2\), ceria) showed interesting properties. It is a semiconductor with a lower band-gap (2.7–2.8 eV) than TiO\(_2\) (3.0–3.2 eV) which allows to better exploit the solar irradiation (more interesting for large scale wastewater treatments). Moreover, its redox properties (coexistence of the Ce\(^{4+}\) and Ce\(^{3+}\) ions as defective sites) also take part in Fenton-like processes (reactions (1-3)) [17, 18]:

\[
\text{Ce}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Ce}^{4+} + \text{OH}^- + \text{OH} \quad (1)
\]

\[
\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (2)
\]

\[
\text{Ce}^{4+} + \text{HO}_2^- \rightarrow \text{Ce}^{3+} + \text{H}^+ + \text{O}_2 \quad (3)
\]

Furthermore, these reactions can be run at neutral pH [18, 19], whereas the typical Fenton process requires a pH range of 3–4 to avoid the precipitation of the Fe\(^{3+}\) ions, thus limiting its application.

We here investigated the catalytic and the photocatalytic activity of CeO\(_2\)-based materials in the oxidation of the o-phenylphenol (o-p.p.), a largely employed fungicide whose presence, also at low concentration, can induce serious health problems [20, 21]. Different AOPs as photocatalysis, Fenton and photo-Fenton-like were applied, evaluating the effects of the addition of small amounts of WO\(_3\) on ceria. The presence of WO\(_3\) can have beneficial effects, due to its high photo-oxidation ability and the possibility to obtain oxygen-deficient structures (WO\(_3\)) that can facilitate the redox reactions of the Fenton and photo-Fenton-like processes [22]. Noteworthy, the interaction between the CeO\(_2\) and WO\(_3\) was poorly examined in the literature and, at the best of our knowledge, the potential synergism of hybrid AOPs as the photo-Fenton-like reaction for the degradation of pesticides in water, was not yet investigated. The use of an unconventional photocatalyst as the CeO\(_2\)-WO\(_3\) composite and a hybrid AOP could be an innovative and fascinating way to remove the recalcitrant pollutants from water.

2. MATERIALS AND METHOD

Ce(NO\(_3\))\(_3\)-6H\(_2\)O, KOH and H\(_2\)O\(_2\) were purchased from Fluka, hexamethylenetetramine (HMTA) and o-phenylphenol from Merck, Na\(_2\)WO\(_4\)-2H\(_2\)O from Acros Organics. The products were employed as-purchased.

3. EXPERIMENTAL

3.1. Samples Preparation

The bare CeO\(_2\) was synthesized from Ce(NO\(_3\))\(_3\)-6H\(_2\)O by chemical precipitation using KOH (2 M), maintaining a basic pH (8-9). The formed suspension was maintained under stirring at 80°C for 3 h and kept digesting for 1 day. Successively, the as-obtained slurry after the filtration was dried at 80°C for 24 h. The calcination at 350°C for 4 h allowed to obtain the CeO\(_2\) powders.

The bare WO\(_3\) was prepared slightly modifying the procedure reported by Huang et al., [23]. Specifically, the Na\(_2\)WO\(_4\)-2H\(_2\)O was solubilized in water under stirring at 75°C and kept at pH = 1 by addition of concentrated HCl. The as-obtained yellow precipitate was decanted for 24 h, filtered and washed several times. The final thermal treatments were drying at 80°C and calcination at 350°C for 4 h.

Two CeO\(_2\)-WO\(_3\) composites were synthetized through the ceria precipitation mediated with HMTA to obtain the CeO\(_2\)-5%WO\(_3\) and the CeO\(_2\)-10%WO\(_3\) samples. The % refers to weight percentage. The HMTA is necessary to favour a good dispersion of WO\(_3\) on CeO\(_2\) [24]. In particular, the as-prepared WO\(_3\) powders were dispersed in an HMTA solution (2·10\(^{-4}\) M) and then a solution of Ce(NO\(_3\))\(_3\)-6H\(_2\)O and KOH was added following the same procedure described for the bare CeO\(_2\) preparation. The powders were dried at 80°C and calcined at 350°C for 4 h.

3.2. Characterization Measurements

The Raman measurements were made with the instrument and the experimental set-up reported in the ref. [24].

The UV-vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) was made using a Cary 60 spectrometer. The band-gap energies (\(E_g\)) of the materials were assessed by graphing the modified Kubelka-Munk function vs. the exciting light energy [17, 18].

The BET surface areas of the catalysts were measured by N\(_2\) adsorption-desorption measurements with a ThermoQuest Sorptomatic series 1990 instrument. The powders were outgassed for 12 h at 120°C.

The transmission electron microscopy (TEM) was performed using a Jeol JEM 2100F operating at 200 kV. The evaluation of the average particle diameter size was made following the procedures reported by Fiorenza et al., [24].

The XPS measurements were made with a K-Alpha™ X-ray photoelectron spectrometer. The C (1s) peak at 284.9 eV (due to the adventitious carbon) was used as a reference.

3.3. (Photo)Catalytic Measurements

The photocatalytic tests were made with a lamp that simulates the solar radiation (OSRAM Vitalux 300W, 10.7 mW/cm\(^2\)) irradiating a home-made jacketed Pyrex batch reactor, kept at 25°C. 50 mg of catalyst were suspended in 50 mL of o-p.p. solution (1·10\(^{-4}\) M). The mixture was stirred for 120 min in the dark to achieve the adsorption/desorption equilibrium. During the measurements, aliquots of the suspension were withdrawn at a given time interval to evaluate the o-p.p. concentration by means of Jasco V-730.
UV–vis spectrophotometer. The pesticide degradation was evaluated by following the absorbance peaks at 282 nm in the Lambert–Beer regime, plotting the C/C₀ ratio as a function of time t, where C is the concentration of the pesticide at the time t, and C₀ is the starting concentration of the contaminant.

The Fenton-like reaction was performed with the same apparatus described above, adding 5 mL of hydrogen peroxide (3%, 0.9 M) in the batch reactor without irradiation. On the contrary, for the photo-Fenton-like tests, the reaction mixture was also irradiated with the solar lamp. For the usability tests, after each run, the sample was filtered, centrifugated, washed with demineralized water, dried overnight at 60°C and re-used. In all the (photo) catalytic experiments, the relative standard error (RSE) was 1%, i.e., within the symbol size. The degradation products were analyzed with a quadrupole mass spectrometer.

4. RESULTS AND DISCUSSION

4.1. Structural and Morphological Properties

The Raman spectra of the examined materials are reported in the (Fig. 1). The main vibrational mode of CeO₂ at 461 cm⁻¹ is assigned to the F₂g mode of the fluorite-like structure. This peak was also present in the CeO₂-5%WO₃ and in the CeO₂-10%WO₃ sample, whereas the peak at 1060 cm⁻¹, clearly visible only in the bare CeO₂, can be related to the second-order longitudinal optical mode [25, 26]. Interestingly, the main vibrational modes of tungsten trioxide at 718 and 807 cm⁻¹, attributed to the stretching of O-W-O of the bridging oxygens [27, 28] were present in the CeO₂-10%WO₃ sample, whereas the same signals were not present in the sample having the low amount of WO₃. This can be ascribed to the lower concentration of WO₃ on CeO₂. However, it is possible to note in the CeO₂-5%WO₃ spectrum the peak at 139 cm⁻¹ assigned to the lattice vibrations of WO₃ [29].

The Raman bands at 269 and 321 cm⁻¹ of WO₃ assigned to the δ(O-W-O) deformation vibrations were present also in the CeO₂-10%WO₃, suggesting in this sample the presence of both stoichiometric and defective WO₃ [30].

The TEM images of CeO₂-5%WO₃ and CeO₂-10%WO₃ with their diameter particle size distribution are depicted in the (Fig. 2). The boundary interaction among the CeO₂ and the WO₃ are visible in both samples. In particular, considering the d-spacing values, the interface was formed among the (111) and the (2 0 0) planes of cerium and tungsten oxides, respectively [23, 31]. Interestingly, whereas the mean diameter size of CeO₂ remained the same in both the catalysts (18 nm) a higher amount of WO₃ led to a decrease of the mean size of this hosted oxide, from 7 nm of the CeO₂-5%WO₃ sample to 4.5 nm of the CeO₂-10%WO₃. Probably the contemporaneous presence of the HMTA and the salt precursor of WO₃ in higher amount favor the formation of smaller size WO₃ particles compared to the CeO₂-5%WO₃, also facilitating its dispersion on CeO₂ [32, 33]. However, the presence of aggregates of CeO₂ and WO₃ cannot be fully excluded.

The UV-DRS of the examined catalysts are displayed in the (Fig. 3) and the estimated optical band gap calculated by means of the modified Kubelka-Munk function are reported in the Table 1.

The bare WO₃ showed the most red-shifted reflectance spectrum (Fig. 3) and, as a consequence, the lowest E_g (2.58 eV). Among the CeO₂-WO₃ composites, the sample with the highest amount of tungsten trioxide exhibited a lower band gap with respect to the CeO₂-5%WO₃ (Table 1), with a E_g (2.64 eV) intermediate between the bare CeO₂ (2.81 eV) and WO₃ (2.58 eV). Probably, the increase of the WO₃ amount on CeO₂ favoured the red-shift compared to bare CeO₂, thus decreasing the band gap of the mixed oxides.

Another interesting effect due to the presence of WO₃ as hosted oxide of CeO₂ was the increase of the surface area. As it is possible to note from Table 1, the presence of WO₃ increased the surface area from 78 m²/g of bare CeO₂ to 95 m²/g of CeO₂-10%WO₃. This can be related to the good dispersion of WO₃ on CeO₂ favoured by the presence of HMTA during the synthesis of the composites [24], as also confirmed by TEM measurements. Moreover, the smaller size of WO₃ in CeO₂-10%WO₃ compared to CeO₂-5%WO₃ (Fig. 2) can further explain its higher surface area. The bare WO₃ showed the lowest surface area according to the literature when the chemical precipitation of Na₂WO₄ was employed as procedure for the preparation of WO₃ [23].

The surface features of the as-synthesized samples were examined by means of XPS and summarized in the Table 2.

In all the samples the six signals in the Ce 3d region were due to the 5/2 (first three signals) and the 3/2 (the others) states. The presence of the Ce³⁺ was usually related to the peak at binding energy (BE) of 916.5–917.0 eV, whereas the Ce⁴⁺ was associated to the features (typically with low intensity) at BE of 885.4-886.4 eV and 904.3 and 905.6 (sometimes overlapped to the signals at about 901 and 907 eV) [34].

In the CeO₂-5%WO₃ composite the ratio between the cerium ions remained substantially the same of the bare CeO₂,
whereas a slight enhancement was verified with the CeO$_2$-10%WO$_3$ sample (Table 2). This can be correlated to a stronger electronic interaction between the cerium and the tungsten ions facilitated by the high dispersion of the WO$_3$ on CeO$_2$ in this sample, as verified by TEM.

A further indication of the establishment of this interaction was the shift at higher BE (about 0.3 eV) of the Ce signals of CeO$_2$-10%WO$_3$ compared to CeO$_2$ (Table 2) justified by the higher electronegativity of W (2.3) with respect to Ce (1.1) [35]. In the W 4f region, the signal of the WO$_3$-based samples revealed the presence of W$^{6+}$ oxidation state [36], whereas a deep analysis of the spectra of the CeO$_2$-10%WO$_3$ (Fig. 4) pointed to the presence of different components as the Ce 5s states (37.0 eV), the W 4f$_{5/2}$ and W 4f$_{7/2}$ (BE of 35.8 and 38.0 eV, respectively). The signals at 34.3-36.5 eV (not present in the CeO$_2$-5%WO$_3$ sample and with very low intensity in the bare WO$_3$) were associated with the non-stoichiometric W species [37]. The presence of these defective sites (also detected by Raman spectroscopy in this sample) is another proof of the synergy and the electronic interaction between the Ce and the W ions in the CeO$_2$-10%WO$_3$ sample.

4.2. (Photo)catalytic Performance

The results of the photocatalytic oxidation of the o-p.p. fungicide after 5 h of solar irradiation are illustrated in the (Fig. 5A). The CeO$_2$-10%WO$_3$ sample showed the best photocactivity with a degradation percentage of 30% ($C/C_0=0.7$). The composite with the lower amount of tungsten trioxide degraded up to 17%, whereas a low photocactivity was detected with the bare oxides.
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Fig. (3). UV-vis Reflectance spectra of the examined catalysts. In the inset, the estimation of the optical band gap through the modified Kubelka-Munk function (CeO$_2$-10%WO$_3$ was chosen as a representative sample). (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Table 1. Band gap energies ($E_g$) and surface areas of the as-synthesized samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (eV)</th>
<th>BET Surface Area ($m^2/g$)</th>
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<tbody>
<tr>
<td>CeO$_2$</td>
<td>2.81</td>
<td>78</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>2.58</td>
<td>17</td>
</tr>
<tr>
<td>CeO$_2$-5%WO$_3$</td>
<td>2.83</td>
<td>84</td>
</tr>
<tr>
<td>CeO$_2$-10%WO$_3$</td>
<td>2.64</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 2. Surface properties of the examined samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ce 3d (eV)</th>
<th>Ce$^{3+}$/Ce$^{4+}$ Ratio</th>
<th>W 4f (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>882.3, 888.5, 898.4, 900.7, 907.1, 916.6</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>/</td>
<td>/</td>
<td>35.8,38.0</td>
</tr>
<tr>
<td>CeO$_2$-5%WO$_3$</td>
<td>882.3, 888.7, 898.5, 900.6, 906.9, 916.6</td>
<td>0.18</td>
<td>35.8,38.0</td>
</tr>
<tr>
<td>CeO$_2$-10%WO$_3$</td>
<td>882.6, 888.9, 898.8, 900.9, 907.7, 916.9</td>
<td>0.22</td>
<td>35.8,38.0</td>
</tr>
</tbody>
</table>

Fig. (4). XPS spectra and the deconvolution components (cyan, orange and violet line) of the CeO$_2$-10%WO$_3$ sample in the W 4f region. The red and the black line refers to the sum of all the Gaussian components and to the experimental spectra, respectively. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

In the Fenton-like reaction (Fig. 5B) performed with the addition of H$_2$O$_2$ (3%) without irradiation, only a slight variation of the initial concentration of the pesticide was verified after 5 h of test with CeO$_2$-10%WO$_3$ (C/C$_0$= 0.93). As explained in the introduction (reactions 1-3), with CeO$_2$-based materials, the presence of the Ce$^{3+}$ species on the surface of CeO$_2$ is necessary to promote the Fenton-like process. The XPS measurements (Table 2) pointed to a little increase of the Ce$^{3+}$/Ce$^{4+}$ ratio in the CeO$_2$-10%WO$_3$ compared to the bare ceria, thus explaining the tiny variation of the catalytic activity in this reaction with this catalyst.

The simultaneous use of the hydrogen peroxide and the solar irradiation led to a positive effect in the hybrid AOP, i.e., the photo-Fenton-like reaction (Fig. 5C). In this condition, indeed, the sample with the highest amount of WO$_3$ allowed to reach 65% of the o.p.p. degradation, higher than 37% of CeO$_2$-5%WO$_3$, 19% of pure CeO$_2$ and 8% of bare WO$_3$. In particular, as reported in the literature [18, 38], the increase of the activity of the CeO$_2$-based samples was ascribed, to the interaction with some solar photons that, owning an energy higher than the band-gap of these materials (Table 1, $E_g$ in the range 2.64-2.8 eV, i.e., photons with $\lambda \leq 469$ nm), allowed the formation of the Ce$^{3+}$ species with the loss of surface oxygen of ceria-based materials (reaction 4):

$$2 \text{CeO}_2 + \text{hv (E } \geq E_g) \rightarrow \text{CeO}_2^{+} + 1/2 \text{O}_2 \quad (4)$$

In this way, the increase of the formation of Ce$^{3+}$ combined with the photoactivity of ceria, boosted the degradation of the pesticide. Noteworthy, the reaction (4) also occurred during the photocatalytic test, whereas the addition of the H$_2$O$_2$ is necessary to favour the enhancement of the hydroxyl radicals formation, able to improve the oxidation reaction [39].
In accordance with the literature [21, 40, 41], the photocatalytic removal of the o-phenylphenol under solar or visible light irradiation is characterized by the formation of several by-products, the main ones being ethyl phenethyl ether and phenyl acetaldehyde. The same intermediates were detected in this study under both the photocatalytic and the photo-Fenton-like conditions. As reported, the reaction mechanism involves the formation of an intermediate adduct between o-p.p. and \( \cdot \text{OH} \) radicals [40, 42]. This compound was easily oxidized by the holes and by the other \( \cdot \text{OH} \) radicals generated during both the photocatalytic and the photo-Fenton-like reactions. This leads to the aromatic ring cleavage with partial mineralization and formation of the phenethyl intermediates [41, 43].

The high activity of the CeO\(_2\)-10\%WO\(_3\) sample compared to the other samples can be ascribed to the strong interaction of the CeO\(_2\) and WO\(_3\) particularly prominent with this amount of the hosted oxide, as confirmed by XPS, that also favoured a good dispersion and a decrease of the particles diameter of WO\(_3\) (see TEM measurements) with an increase of the surface area (Table 1). It is important to note that a higher amount of WO\(_3\) (15 or 20 wt\%, data not shown) led to a detrimental effect with a degradation percentage lower of 20% employing the best approach, i.e., the photo-Fenton-like reaction. This negative effect can be due, similarly to other semiconductor-based composites, to the partial or the total coverage of the surface of the main oxide due to progressive deposition of the hosted oxide [44].

The peculiar interface between the cerium and tungsten oxides exploited with the CeO\(_2\)-10\%WO\(_3\) composite was boosted in the photo-Fenton-like process. The electronic interaction between the Ce ions and the W sites, present also as defective centres (Fig. 4), favoured the further formation of Ce\(^{3+}\) centres with an additional synergism that led to sensibly increase the performance of this sample.

To verify the changes in the surface state of this composite after the photo-Fenton-like test, XPS characterization was performed and compared to the spectra obtained with the fresh catalyst. The comparison of the XPS spectra in the Ce 3d region shows the increase of the Ce\(^{3+}\) species with respect to the as-synthesized sample (Fig. 6).

Indeed, after the test the peak at 885 eV was more pronounced, and this is a typical fingerprint of the presence of Ce\(^{3+}\) state, as also the change in the ratio of the signals at
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The Ce$^{3+}$/Ce$^{4+}$ ratio doubles from 0.22 of the as-synthesized composite to 0.41 of the sample after the test.

Furthermore, the shift of 0.4 eV at higher binding energy of all the Ce peaks in the used sample is another indication of the strong interaction between the Ce and W ions that allowed to conspicuously improve the catalytic activity of this catalyst in the removal of the fungicide under the solar photo-Fenton-like conditions.

Table 3. Comparison of some photocatalysts used for the o-p.p. degradation.

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<tbody>
<tr>
<td>CeO$_2$-10%WO$_3$</td>
<td>photo-Fenton</td>
<td>[o-p.p.] 10$^{-4}$ M; solar lamp 107 W/m$^2$; 5 h irradiation</td>
<td>65</td>
<td>this work</td>
</tr>
<tr>
<td>N1.2%M-MI TiO$_2$/o-p.p.</td>
<td>photocatalysis</td>
<td>[o-p.p.] 10$^{-4}$ M; solar simulator 1000 W/m$^2$; 4 h irradiation</td>
<td>46</td>
<td>[21]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>photocatalysis</td>
<td>[o-p.p.] 5·10$^{-4}$ M; UV lamp 365 nm, 4·10$^{15}$ photons cm$^{-2}$s$^{-1}$; 8 h irradiation</td>
<td>89</td>
<td>[40]</td>
</tr>
<tr>
<td>Bi$_2$O$_3$/Bi$_2$O$_2$CO$_3$</td>
<td>photocatalysis</td>
<td>[o-p.p.] 10$^{-4}$ M; 1000 W Xe lamp; 1 h irradiation</td>
<td>90</td>
<td>[41]</td>
</tr>
<tr>
<td>Bi$_4$O$_6$I$_3$Br$_1$</td>
<td>photocatalysis</td>
<td>[o-p.p.] 10$^{-4}$ M; 500 W halogen lamp; 1 h irradiation</td>
<td>95</td>
<td>[43]</td>
</tr>
</tbody>
</table>

898 and 901 eV [45]. The Ce$^{3+}$/Ce$^{4+}$ ratio doubles from 0.22 of the as-synthesized composite to 0.41 of the sample after the test.

**Fig. (6).** XPS of the CeO$_2$-10%WO$_3$ sample in the Ce 3d region; comparison before (olive line) and after (wine line) the photo-Fenton-like test. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

**Fig. (7).** Stability test of CeO$_2$-10%WO$_3$ in 5 consecutive runs of the solar photo-Fenton like reaction. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Finally, the stability of the CeO$_2$-10%WO$_3$ composite was good after 5 consecutive runs of the solar photo-Fenton-like reaction (Fig. 7) with a negligible decrease of activity. The o-p.p. degradation, indeed, varies from the 65% of the first run to the 61% of the fifth run. At the end of each run the sample was centrifugated, washed with demineralized water, dried overnight at 60°C and finally re-used. The in-
crease of the amount of Ce$^{3+}$ species (as detected by XPS, Fig. 6) of the CeO$_2$-10%WO$_3$ sample did not significantly affect the stability of the catalyst.

Table 3 compares the performance of different photocatalysts reported in the literature for the o-p.p. degradation. It can be noted that under solar irradiation and with the photo-Fenton approach, the o-p.p. degradation percentages of the CeO$_2$-10%WO$_3$ composite are comparable to or better than TiO$_2$-based samples, whereas higher photoactivity was measured under UV irradiation or employing BiO$_x$-based composites.

CONCLUSION

An efficient heterojunction was formed between CeO$_2$ and WO$_3$ using the precipitation technique mediated with the HMTA surfactant. The CeO$_2$-10%WO$_3$ composite showed the best performance in the removal of the o-phenylphenol fungicide with the photo-Fenton-like process. This reaction was favoured by the presence of the Ce$^{3+}$ sites, whose formation was promoted by the high interaction between the Ce and the W ions. The unconventional CeO$_2$-WO$_3$ composite can be a promising and versatile catalyst for the removal of emerging pollutants from water.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

FUNDING

None.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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REFERENCES

http://dx.doi.org/10.1007/s13369-020-04446-1

http://dx.doi.org/10.3390/molecules22071070 PMID: 28672875

http://dx.doi.org/10.1016/j.jhydrol.2009.12.012

http://dx.doi.org/10.1002/cctc.201902081

http://dx.doi.org/10.1016/j.cej.2020.124302

http://dx.doi.org/10.1016/j.jphotochem.2016.01.024

http://dx.doi.org/10.1016/j.jiec.2019.12.021

http://dx.doi.org/10.1016/j.chemosphere.2018.07.170 PMID: 30081220

http://dx.doi.org/10.1016/j.jphotochem.2019.111872

http://dx.doi.org/10.1016/j.jjche.2013.10.011

http://dx.doi.org/10.1016/j.apcata.2010.05.004

http://dx.doi.org/10.1016/j.scitotenv.2020.143258 PMID: 33190879

http://dx.doi.org/10.1016/j.cattod.2019.11.028

http://dx.doi.org/10.1016/j.scitotenv.2020.143852


http://dx.doi.org/10.1021/es8001508 PMID: 18678042

http://dx.doi.org/10.3390/catal10040446

http://dx.doi.org/10.1016/j.jcis.2019.09.079 PMID: 31586736

http://dx.doi.org/10.1016/j.apcata.2014.10.036
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