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Tungsten oxide: a catalyst worth studying for the abatement and decontamination of chemical warfare agents

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ABSTRACT

Tungsten(VI) oxide, WO_3 , was studied and used as a heterogeneous catalyst for the liquid-phase oxidative abatement and solid-phase decontamination of simulants of chemical warfare agents, CWAs. The catalytic performance of WO_3 was compared to the one of a soluble W-containing model catalyst, W(IV)-heptaisobutyl polyhedral oligomeric silsesquioxane, W-POSS. In liquid-phase abatement tests, WO_3 promoted a complete degradation of the toxic agent simulant within 24 h, in the presence of aqueous hydrogen peroxide, at room temperature. In solid-phase decontamination tests, when WO_3 was mixed with sodium perborate as a solid oxidant, it was also tested in the decontamination of a cotton textile support from organosulfide and organophosphonate agents (simulants of blistering and nerve CWAs, respectively), showing promising performances comparable to, or sometimes better than, a nanostructured TiO_2 catalyst, taken as a reference material. The environmental impact of the WO_3 catalyst was assessed on bioluminescent *Photobacterium leiognathi* Sh1 bacteria, over which no acute nor chronic detrimental effects were recorded. Then, when in contact with a vegetable species such as *Phaseolus vulgaris* L. (common bean), WO_3 did not cause damage to the photosynthetic apparatus of the plant, whereas a clear inhibition of the seed germination was evidenced.

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1. Introduction


Chemical warfare agents, CWAs are typically classified according to their physiopathological effects on organisms (Guidotti & Trifirò, 2015). Among these toxic chemicals, it is possible to recall widely known blistering agents, such as *sulfur mustard* or yperite (*bis*-(2-chloroethyl)sulfide) and lewisite (2-chloroethenylarsonous dichloride), as well as the neurotoxic agents *sarin* (propan-2-yl methylphosphonofluoridate) and *so man* (3,3-dimethylbutan-2-yl methylphosphonofluoridate) (McCauley, 2015; Szinicz, 2005). Recently, the attention on CWAs was revived after the threat and periodic use of chemical toxic agents in Syrian civil war, with the problems connected to their safe destruction and the risk of diffusion of residual stockpiles of chemical weapons into terrorists' hands (Fischer, Blum, Alwan, & Forman, 2017).

Typical processes or the destruction and abatement of CWAs are based on drastic degradation methods, such

as thermal destruction and hydrolysis reactions, relying on the use of concentrated alkaline solutions and/or total oxidation processes using strong oxidants, mainly in the presence of active chlorine sources (such as NaOCl , $\text{Ca}(\text{OCl})_2$ and dichloroisocyanurate salts) (Beer Singh, Prasad, Pandey, Danikhel, & Vijayaraghavan, 2010; Kim, Tsay, Atwood, & Churchill, 2011; Miskelly, 2004). These non-catalytic approaches are often associated with high energy consumption, large over-stoichiometric amounts of reactants, relevant costs and a non-negligible environmental impact.

A valid alternative to these conventional chemical abatement strategies is the use of heterogeneous catalysts for the selective oxidation of CWAs into partially or fully oxidised non-toxic (or far less toxic) products (Bromberg, Creasy, McGarvey, Wilusz, & Hatton, 2015; Jang, Kim, Tsay, Atwood, & Churchill, 2015; Oudejans et al., 2016; Smith, 2008; Wagner, 2011, 2015). In the literature,

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different classes of materials, such as supported vanadium and molybdenum polyoxometalates (POMs), as well as iron-, tungsten- or niobium-containing POMs (Gall, Hill, & Walker, 1996; Kinnan, Creasy, Fullmer, Schreuder-Gibson, & Nyman, 2014; Mizrahi, Saphier, & Columbus, 2010; Okun, Anderson, & Hill, 2003), porous oxides, such as zeolites and mesoporous silicas (Kholdeeva, 2014; Livingston & Landry, 2008), have been explored for catalytic decomposition of CWAs. Most of them showed, as a matter of example, very good conversion and selectivity in the oxidation reaction of organic sulfides into sulfoxides, whose reactivity mimics the oxidative abatement and detoxification of blistering warfare agents. More recently, layered solids and especially clays (Carniato, Bisio, Psaro, Marchese, & Guidotti, 2014; Michalkova et al., 2006; Plachá et al., 2014) or nanostructured inorganic metal oxides, such as aluminum oxide (Al_2O_3), zinc oxide (ZnO), magnesium oxide (MgO) and titanium oxide (TiO_2), were widely studied and used with good results in CWA oxidation and/or degradation reactions (Beer Singh et al., 2010; Bisio et al., 2016; Neatu et al., 2010; Zafrani et al., 2011). The catalytic performance of inorganic oxides in the decontamination of hazardous chemicals is, to a large extent, related to their form, size and shape. When they are bulk aggregates or macroscopic powders, they are able to remove the hazardous contaminant quite efficiently by physical adsorption, but, then, they can scarcely degrade and catalytically convert it into non-toxic by-products (Mawhinney, Rossin, Gerhart, & Yates, 1999; Prasad, Ramacharyulu, Kumar, Ganesan, & Singh, 2012). On the other hand, when the inorganic oxides are dispersed at nanosized level, the large presence of defective and highly reactive sites at the surface of the solid gives rise to acid-base and/or redox properties and hence to enhanced hydrolytic and/or degradation capabilities (Guidotti, Evangelisti, Rossodivita, & Ranghieri, 2014). These features, strictly related to both the physicochemical nature of the metal oxide and its surface properties, can therefore be thoroughly tuned and directly exploited for a successful and safe abatement of CWAs (Kleinhammes

et al., 2005; Prasad et al., 2011; Trubitsyn & Vorontsov, 2005).

Tungsten oxide-modified titanate nanotubes have been used successfully as photocatalytic systems for the removal of chemical warfare agents from textiles (Grandcolas, Louvet, Keller, & Keller, 2009; Grandcolas et al., 2011). Tungsten-containing Keggin-type POMs have been tested with some success in the degradation of *sarin* and VX nerve agents too (Mizrahi et al., 2010). However, in general, bulk tungsten trioxide and related compounds have been scarcely taken in consideration as suitable catalysts for oxidative abatement reactions (Kuo, 2010; Okun & Hill, 2004).

In the present work, a non-nanostructured and commercially available tungsten trioxide, WO_3 , was used for the first time as a heterogeneous catalyst for the liquid-phase abatement and solid-phase decontamination of (2-chloroethyl)ethylsulfide, CEES, and dimethylmethylphosphonate, DMMP, as CWA simulants. These compounds possess indeed distinctive functional groups found in blistering and nerve agents: the $-\text{S}-\text{CH}_2-\text{CH}_2-\text{Cl}$ moiety and the $\text{CH}_3-(\text{P}=\text{O})$ group, respectively. They therefore show a chemical reactivity similar to one of sulfur mustard (HD agent) and organophosphonic nerve agents (G agents), but with a remarkably reduced toxicity (Bartelt-Hunt, Knappe, & Barlaz, 2008).

The performance of WO_3 was compared with the one of a tungsten-based molecular complex, W(IV)-heptaisobutyl-POSS, featuring a polyhedral oligomeric silsesquioxane (POSS) framework (Pescarmona & Maschmeyer, 2001), specifically prepared and used as a model soluble catalyst (Figure 1).

Abatement tests were performed in liquid phase, in a batch reactor, mimicking the destruction and degradation of controlled amounts of CWA stockpiles in a confined environment. Solid-phase decontamination tests, on the contrary, were carried out on a sample of textile support, under solvent-less conditions fully comparable to real-life use, at room temperature, mimicking the decontamination of protective clothing from liquid CWAs. In

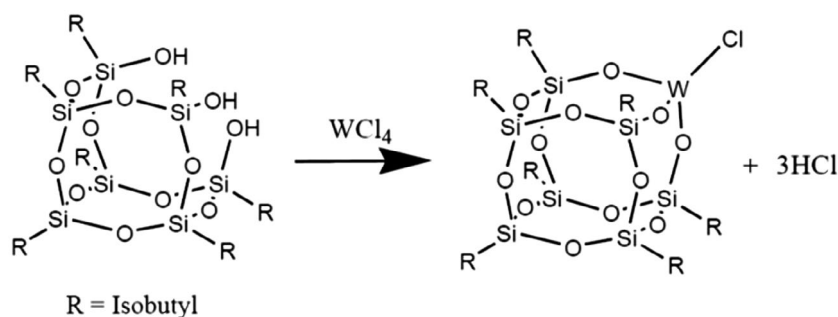


Figure 1. Schematic representation of the corner-capping reaction of partially condensed isobutyl POSS with WCl_4 .

each of these experiments, the oxidative degradation of the hazardous contaminant was achieved by adding to the reaction mixture a chlorine-free environmentally friendly oxidant, such as aqueous hydrogen peroxide, in liquid-phase tests, and sodium perborate or urea-hydrogen peroxide (UHP) adduct in solid-phase ones.

Finally, aiming at a real on-field use, where a total-loss dispersion of solid decontamination mixtures is likely, the potential impact of the catalysts on the environment was evaluated by three main kinds of biotests, as rapid, cost-effective and sensitive screening tools: (i) the marine bioluminescent bacterium, *P. leiognathi* Sh1, isolated from Azov Sea, was utilised as a target organism to assess the direct toxic impact on living organisms (Katsev, 2014; Kuryanov, Chupakhina, Shapovalova, Katsev, & Chirva, 2011); (ii) the potential mutagenic properties of the solids and their ability to generate toxic oxygen radicals were evaluated by luminescent bioreporter strains of *Escherichia coli* MG1655, with the lux CDABE operon from *Photorhabdus luminescens* (Chugunova et al., 2016, 2015; Zavilgelsky, Kotova, Yu, & Manukhov, 2007); and (iii) the potential detrimental impact of the solids on vegetable plants was evaluated by studying the effects on the chlorophyll fluorescence and on germination parameters on *P. vulgaris* L., as a model plant (common bean plants) (Maxwell & Johnson, 2000).

2. Materials and methods

2.1. Materials

W-heptaisobutyl POSS (W-POSS): the sample was prepared adapting the procedure reported by Smet *et al.* (Smet et al., 1998). Briefly, the molecule was synthesised by the corner-capping reaction of an equimolar amount of partially condensed isobutyl POSS (Hybrid Plastic, SO1450) with tungsten(IV) chloride (WCl_4 , Sigma) in benzene solvent at reflux temperature. The reaction was carried out for 6 h, under vigorous stirring. The sample was then filtered in order to remove the unreacted precursor and the solution was dried under vacuum under mild heating in order to remove the solvent and obtain a powdery product. The product will be hereafter named W-POSS.

Tungsten (VI) trioxide, WO_3 , was purchased from Sigma-Aldrich (95410). The sample possesses a specific surface area of $22 \text{ m}^2 \text{ g}^{-1}$, with an irregular non-ordered broadly dispersed porous feature, mainly due to particle aggregation.

Nanometer-sized titanium dioxide, TiO_2 material was prepared as previously detailed (Bisio et al., 2016).

Sodium perborate tetrahydrate (Sigma-Aldrich; purum) and urea-hydrogen peroxide adduct (UHP; Sigma-Aldrich; 15–17% active oxygen basis) were finely ground with pestle and mortar prior to use.

2.2. Characterisation

- X-ray diffraction (XRD) profiles were collected on a ARL XTRA48 diffractometer equipped with Cu K α radiation ($\lambda = 1.54062 \text{ \AA}$).
- Diffuse reflectance UV–vis (DR-UV–vis) spectra were recorded on a Perkin Elmer Lambda 900 spectrometer equipped with an integrating sphere accessory. The samples were dispersed in barium sulfate matrix (20 wt.%) and placed in a hand-made quartz cell.
- Scanning electron microscopy (SEM) images were obtained by a LEO 1450 VP instrument. Prior to the analysis, the samples were coated with a gold layer of few nanometers in order to promote the surface conductivity.
- Infrared (IR) spectra were collected on a Bruker Equinox 55 (resolution of 4 cm^{-1}) equipped with a pyroelectric DTGS detector. The samples, diluted in a KBr matrix (*ca.* 20 wt%) and reduced into the form of self-supporting pellets, were placed into an IR cell equipped with KBr windows.
- Raman spectra have been recorded on as-prepared powders using a Bruker RFS 100 FT spectrophotometer with a Nd $^{3+}$ YAG laser source ($k = 1064 \text{ nm}$) and a laser power of 50 mW. Two thousand scans were collected for each spectrum.
- High-resolution transmission electron microscopy (HR-TEM) and high angular annular dark field SEM (HAADF-STEM) images were collected by a ZEISS LIBRA200FE microscope equipped with a 200 kV FEG source. The finely ground powder samples were ultrasonically dispersed in isopropyl alcohol and then the suspension was dropped onto a holey carbon-coated copper grid (300 mesh), by evaporating the solvent.

2.3. Catalytic tests

2.3.1. Catalytic oxidative abatement

In the tests for the catalytic oxidative abatement of the blister agent simulant (2-chloroethyl)ethyl sulfide (CEES; 98% Aldrich), a 14 mM solution of CEES in *n*-heptane (HPLC grade; Fluka), containing 30 wt.% aqueous hydrogen peroxide (70 mM; Aldrich) and 20.0 mg of solid catalyst (WO_3 , W-POSS or TiO_2), was reacted at 25 °C, the overall volume of the mixture being 20.0 mL. Samples (0.1 mL aliquots) of the reaction mixture were withdrawn at regular intervals (typically 0, 1, 2, 3, 4, 5, 20 and 24 h) during the 24-h-long reaction time. The gradual consumption of CEES was followed by UV–vis spectroscopy in transmission mode (3.0 mL quartz cuvette) on a Perkin Elmer Lambda 900 spectrometer, by monitoring

the characteristic absorption maximum at 206 nm. Each conversion profile curve is the average of at least two tests.

2.3.2. Catalytic oxidative decontamination

The second series of tests for the catalytic oxidative decontamination of fabric from (2-chloroethyl)ethyl sulfide, CEES, or dimethylmethylphosphonate, DMMP, was performed as previously described in detail (Carniato et al., 2014). Briefly, on a cotton textile sample (9 cm²; 200 mg), 0.17 mmol of either CEES or DMMP was deposited and then covered by a solid formulation composed by the catalyst to be tested (WO₃ or TiO₂) and a solid oxidant (sodium perborate tetrahydrate or urea hydrogen peroxide adduct, UHP). Five milligrams of catalyst plus 5 mg oxidant were used for each test (10 mg in total of solid decontamination formulation). After 1 min, the textile was treated with 20 µL of deionised water. In some cases, the contaminated area containing the solid mixture was thoroughly brushed with a soft brush (size: 1 × 3 cm). The decontamination efficiency was measured by collecting the off-vapours 2.0 cm perpendicularly above the contamination test area and by means of an on-field open-loop ion mobility spectrometer (CHEMPRO100i, Environics Oy). The data for each catalytic decontamination test were collected from at least five replicas over different specimens of the same batch of cotton textile fabric. Reference tests in the absence of the solid catalyst and/or in the absence of the chemical agent simulant were performed as well.

2.4. Environmental tests

2.4.1. Bioluminescence inhibition tests

The ecotoxicological properties of tungsten-containing materials and related compounds were evaluated by bioluminescence inhibition tests, based on Azov Sea test-bacterium *P. leiognathi* Sh1, according to protocols previously described (Katsev, 2014). The tests were replicated at least three times.

For agar diffusion test on *P. leiognathi* Sh1 growth and bioluminescence, a Petri dish with a solid nutrient medium (Himedia, India), containing 3% NaCl, was first spread, the night before, onto the *P. leiognathi* Sh1 bacterial culture in the liquid medium. Then 10 mg of the solid catalyst sample (powders of WO₃, TiO₂ and WCl₄) were placed on the agar surface. Petri dish was incubated for 24 h at 27 °C, optimal for bacteria growth, and then observed. Bacterial growth inhibition zones were observed and photographed under daylight conditions. Conversely, bioluminescence inhibition zones were observed under dark conditions. Photographic pictures of the glowing bacterial fields with brown inhibition zones were collected on a Canon EOS 600D camera, in automatic mode at maximal resolution (5184 × 3456 pixels).

The mutagenic properties of the solid catalysts and their ability to generate toxic reactive oxygen species (ROS) were analysed by bioluminescent reporter strains, as previously discussed (Chugunova et al., 2015). These recombinant strains, based on *E. coli* MG1655 with the lux CDABE operon, were kindly provided by I. V. Manukhov (Federal State unitary Enterprise, GosNIIGenetica, Moscow, Russia) and include *E. coli* MG1655 (pXen7), *E. coli* MG1655 (pRecA-lux), *E. coli* MG1655 (pColD-lux), *E. coli* MG1655 (pKatG-lux) and *E. coli* MG1655 (pSoxS-lux).

2.4.2. Evaluation of the induction chlorophyll fluorescence

The evaluation of the induction chlorophyll fluorescence (IChF) was carried out on a Floratest fluorometer (Institute of Cybernetics of National Academy of Science, Ukraine) by letting the samples in the dark for 3.0 min before analysis. Sample leaves were taken from identical positions from each plant and the time of measurement was fixed to 160 s. A typical fluorescence intensity curve vs. time is reported in Supplementary Material (Figure S1) and described in detail in previous reports (Starodub et al., 2014).

P. vulgaris L. (common bean) was used as a target vegetable species for the determination of the environmental toxicity. Germination, vigour and induction of chlorophyll fluorescence were measured as key parameters. The intensity of vigour was estimated as the quantity of seeds germinated in the time span of 24 h. Germination is presented as the percentage of seeds, which led to plants after 72 h. In the first step, the seeds were sterilised in a potassium permanganate solution (3 wt.%). Then, they were washed three times with distilled water, deposited (10 units) on a filter paper in Petri dishes and treated with a suspension of the solids to be tested (amounts between 0.5 and 2.0 mg mL⁻¹). The seeds were germinated in an incubator for 72 h at 25 °C, under dark conditions until the appearance of the embryonic root. One seed, humidified by distilled water, was taken as a control. All experiments were replicated at least three times (Sherer & Sarakhan, 2007).

3. Results and Discussion

3.1. Characterisation of the catalytic materials

The tungsten-based catalytic materials were analysed by spectroscopic and microscopic techniques in order to confirm their physicochemical nature. Particular emphasis has been put in the characterisation of W(IV)-heptaisobutyl POSS, W-POSS, that is a non-commercial model compound.

The synthesis of W-POSS was monitored by infrared (IR) spectroscopy in order to evaluate the reaction

evolution and to optimise the synthesis conditions required to obtain W-POSS (data not shown for the sake of brevity). The IR analysis was performed in liquid phase by collecting small amounts of the reaction medium. The IR spectra collected over the time showed a progressive reduction of the intensity of the broad band in the 3400–3100 cm^{-1} range, which was attributed to the stretching modes of the silanol groups of the partially condensed POSS (Carniato et al., 2007). This absorption disappeared almost completely within 4.5 h, thus indicating the closure of the POSS cage promoted by the reaction of the partially condensed POSS and the metal precursor. A scheme of the synthesis procedure is reported in Figure 1.

The presence of W(IV) centres in the structure was evaluated by infrared and Raman spectroscopy (Figure 2). In the FT-IR spectrum of W-POSS (Figure 2(A), (b)) the broad bands at 3250 and 890 cm^{-1} , (Colthup, Daly, & Wiberley, 1990) ascribed to the stretching of O–H and Si–OH groups and typical of partially condensed POSS, were not visible, whereas a new absorption at 900 cm^{-1} , assigned to the stretching of Si–O–W group, appeared. These modifications suggest that the POSS cage was successfully closed through corner-capping reaction with WCl_4 .

The FT-Raman spectrum of the W-POSS collected in the 1000–600 cm^{-1} range (Figure 2(B), (b)) showed a new signal around 900 cm^{-1} due to the stretching mode of W(IV) bound to the POSS cage (Socrates, 2001).

The structural properties of the commercial tungsten oxide sample were evaluated using the powder X-ray diffraction technique. As general feature, the X-ray profile of the sample (Figure 3) shows diffraction peaks located at *ca.* 23.1°, 24.0°, 28.8°, 33.3°, 34.0°, 41.6° and 55.2° of 2θ , which can be directly assigned to the (001), (200), (111),

(021), (220), (221) and (401) planes, respectively, typical of the orthorhombic WO_3 structure (JCPDS No. 20-1324) (Deng, Dou, Li, Gao, & Liu, 2015).

The morphology of the WO_3 sample was also investigated by SEM and high-resolution transmission electron microscopy (HR-TEM; *v. Supplementary Material*). The oxide contains aggregates with irregular organisation (Figure 4(A)) and, at higher magnifications (Figure 4(B)), particles with irregular shape and submicrometer size are visible. However, as evidenced by deeper HR-TEM analysis, only a very minor fraction of the WO_3 bulk material presents sub-structures with size in the order of the tens of nanometers, mainly due to debris-like uneven aggregates (Figure S3).

Finally, particular attention was devoted to the investigation of the coordination state of the tungsten species in W-POSS and WO_3 . DR-UV–visible spectroscopy is an optimal technique to collect information about the site isolation of the tungsten centres and about their chemical surroundings (Figure 5).

The DR-UV–vis spectrum of W-POSS (Figure 5, (a)) showed two main absorptions: the first one at 215 nm and the second one at 265 nm, attributed to the ligand charge transfer between oxygen atoms and the isolated W(IV) sites in tetrahedral and octahedral coordination. Instead, the DR-UV–vis spectrum of WO_3 (Figure 5, (b)) showed three main adsorption bands located at 430, 285 and 255 nm. The adsorption band at 430 nm is due to the electronic transition from the valence band to the conduction band of WO_3 (Irie, Miura, Kamiya, & Hashimoto, 2008). On the other hand, the signals located at lower wavelengths can be attributed to the structure of the conduction electronic band of WO_3 . This is due to the quantum size confinement of electrons and holes in the space

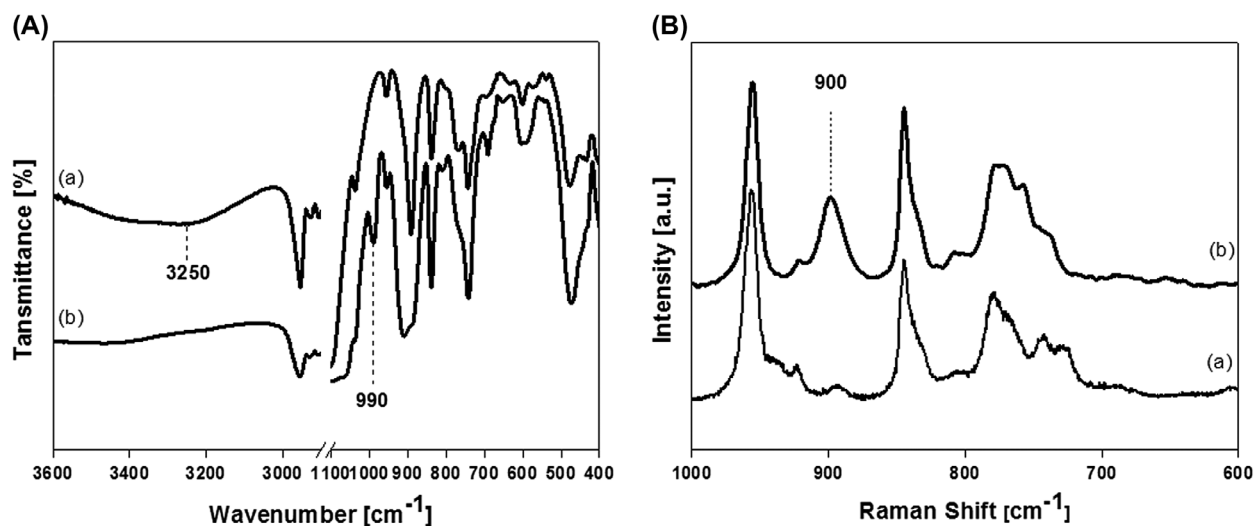


Figure 2. (A) Infrared spectra of partially condensed isobutyl-POSS (a) and W-POSS (b) samples diluted in the KBr matrix (*ca.* 20 wt.%) collected at room temperature. (B) Raman spectra of partially condensed isobutyl-POSS (a) and W-POSS (b) samples.

region defined by the potential barriers (Chen, Zhou, Liu, Liu, & Zou, 2012) and is a clear clue of the bulk nature of the WO_3 species.

The spectroscopic characterisation for W-POSS is fully consistent with the one previously reported for other metal-containing corner-capped polysilsequioxanes. This means that the synthesis of the W-containing model catalyst has been accomplished successfully and that the tungsten sites in W-POSS can be considered as good examples of isolated catalytically active centres, evenly dispersed in a silica matrix. On the contrary, the very low specific surface area ($22 \text{ m}^2 \text{ g}^{-1}$), the neat XRD reflexes and the negligible presence of nanosized particle, from the microscopic analysis, suggest that WO_3 is a conventional bulk inorganic oxide without any significantly defined nanometric structure.

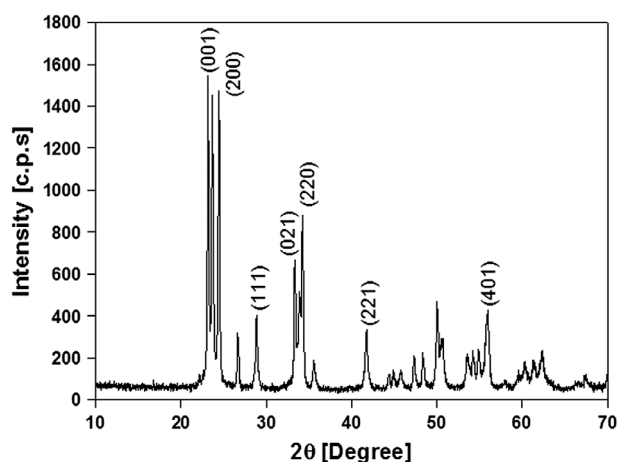


Figure 3. XRD patterns of orthorhombic WO_3 sample.

3.2. Catalytic degradation of blistering agent simulants: the case of CEES

The catalytic properties of W-based materials (WO_3 and W-POSS) in the liquid-phase oxidative abatement of the blistering agent simulant (2-chloroethyl)ethylsulfide, CEES (Bartelt-Hunt et al., 2008) were compared with a nanostructured titanium dioxide, TiO_2 , a material which has already shown interesting properties in the degradation of CWAs and can be thus considered as a benchmark powder catalyst for non-photocatalytically driven decontamination reactions too (Bisio et al., 2016; Prasad et al., 2009; Štengl et al., 2005). The experiments have been performed at room temperature, 25°C , in the presence of 30 wt.% aqueous hydrogen peroxide, in *n*-heptane used as a

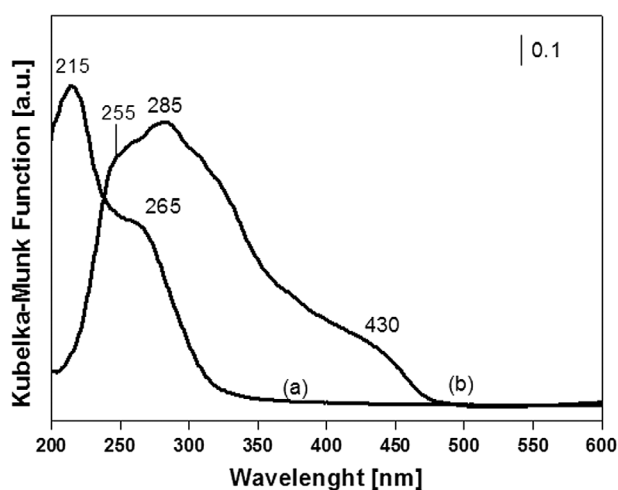


Figure 5. DR-UV-vis spectra of W-POSS (a) and WO_3 (b) samples, diluted in BaSO_4 matrix (20 wt.%), in air and at room temperature.

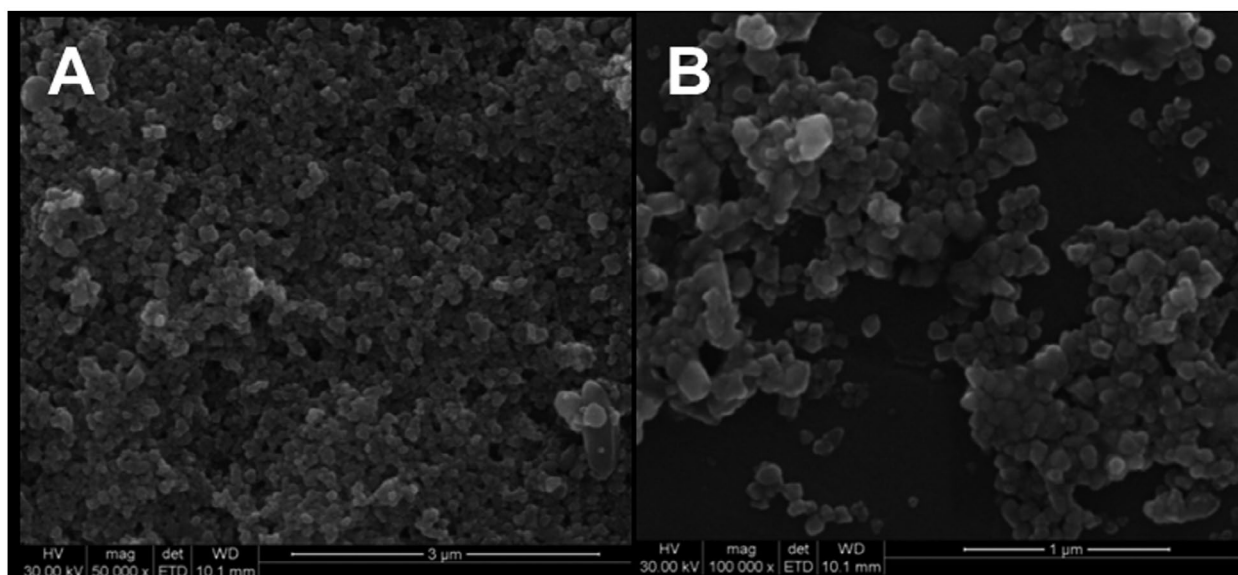


Figure 4. SEM images of WO_3 at magnification 50000 X (A) and 100000 X (B).

solvent. Such conditions are far milder than those typically adopted in the abatement, via oxidative degradation, of residual stockpiles of CWAs in large destruction plants.

The degradation reaction of CEES was followed by monitoring the main UV absorption of the substrate at 206 nm. As a reference, the abatement test was also performed without catalyst (blank condition) and in the presence of aqueous H_2O_2 only. Under these conditions, CEES showed a negligible self-decomposition, with a maximum of 4% degradation after 24 h, likely promoted by a minimal oxidant activity of the oxidant alone (Figure 6).

In the presence of TiO_2 , 44% of CEES abatement was recorded after 5 h and attained 58% after 24 h (Bisio et al., 2016). The WO_3 sample, on the other hand, showed a better catalytic performance in terms of conversion. WO_3 led to 74% of CEES abatement after 5 h and, remarkably, to the complete abatement of the toxic agent simulant after 24 h. In fact, at the end of the reaction time, no residual amounts (i.e. under the detection limit of the spectroscopic technique) of the pristine contaminant were detected in the liquid reaction mixture.

It is worth stressing that the good performance of tungsten-containing catalysts is unprecedented and notable, with respect to nanostructured TiO_2 , which is widely considered as a reference oxide-based material for CWA degradation in the presence of oxidising species. Actually, the abatement reaction proceeds under very mild conditions (ambient temperature), does not need the presence of UV irradiation (as an additional external factor) and is based on the use of a sustainable oxidant (i.e. aqueous hydrogen peroxide, giving rise to water as a unique by-product). In addition, such remarkably promising results have been

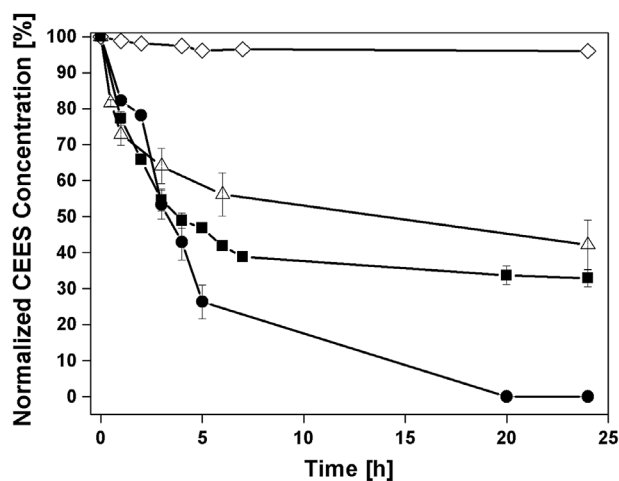


Figure 6. Oxidative abatement of CEES in the presence of hydrogen peroxide over WO_3 (●), W-POSS (■), TiO_2 used as a positive reference catalyst (△), and without solid catalyst (◇). Note: Reaction conditions: 14 mM CEES; 70 mM 30% aq. H_2O_2 ; *n*-heptane; 20 mg catalyst; 25 °C.

obtained over a simple and easily accessible commercial tungsten(VI) trioxide with no additional treatments.

In order to have a deeper insight on how a different chemical environment around tungsten atoms (isolated and evenly dispersed sites vs. bulk inorganic oxide) could affect the catalytic performance in this kind of oxidative abatement, W-POSS was chosen as a model homogeneous catalyst (W-POSS is indeed soluble under reaction conditions) for comparison purposes. W-POSS was able to oxidise 58% of CEES after 5 h and 67% of it after 24 h.

In summary, WO_3 showed a remarkably better performance than W-POSS (Figure 6; maximum CEES abatement ca. 65% vs. > 98% after 24 h, for the former and the latter, respectively). In addition, since WO_3 is not soluble in the reaction mixture, it can be easily separated from the liquid phase, recovered and recycled.

It is hard to attribute the higher conversion values observed over WO_3 solely to the larger amount of W catalytic active sites (ca. 3.3 mg vs. 16 mg of tungsten atoms, that is 18 μmol vs. 87 μmol of W, in 20 mg of catalyst for W-POSS and WO_3 , respectively) in WO_3 than in W-POSS. Indeed, most of the tungsten sites of WO_3 are buried within the structure of micrometer-sized oxide particles (with a rather low specific surface area, i.e. 22 $\text{m}^2 \text{g}^{-1}$ and very large primary crystallites; cf. Figure S3) and hence are not accessible to the reactant molecules. On the contrary, all of the W centres in W-POSS, that is a soluble molecule, are accessible to the substrate and are thus virtually active in the catalytic degradation process. Moreover, the trend of the conversion profiles is comparable, at short reaction times (during the first 3 h), for WO_3 and W-POSS. Then, at longer times, the behaviour of the two systems becomes dissimilar and a complete degradation of CEES is attained over WO_3 only. It is not therefore possible to quantify, at the current stage, the specific activity per tungsten atom site of the two catalytic systems. However, although this aspect might deserve a more specific investigation in further studies, considering the results collected in abatement tests in liquid phase, the commercial WO_3 sample has been selected as the most promising tungsten-containing catalyst for the solid-phase decontamination tests.

3.3. Decontamination from blistering and nerve agent simulants

WO_3 and TiO_2 were then tested as catalysts and components in solid decontamination formulations, mimicking an on-site decontamination protocol, under reaction conditions, as close as possible to the real ones: an aliquot of a mixture composed by the oxide catalyst and a solid oxidant (in 1:1 weight ratio) was deposited over a cotton textile fabric sample, contaminated by few drops (0.17 mmol) of CWA simulant (either CEES or DMMP,

for blistering or nerve agents, respectively). In these tests, either sodium perborate tetrahydrate or urea-hydrogen peroxide adduct (UHP) was selected as a 'solid equivalent' of hydrogen peroxide in the decontamination powder.

The contaminated area on the textile support was treated with the decontamination mixture and, after 1 min, treated with a tiny amount of water (20 μL) and, in some cases, brushed. The small amount of water was added to the powder and to the textile support in order to trigger the oxidising power of the mixture (H_2O_2 -generating oxidant + metal-containing catalyst). The efficiency of *in situ* decontamination and removal of the contaminant was followed and measured by means of a portable on-field CWA detector before and after the removal by brushing. The results are summarised in Figure 7.

In general, the decontamination of the blistering agent simulant, CEES, was easier than the one of the nerve agent simulant, DMMP, as sulphur atoms are typically more readily oxidised by hydrogen peroxide and thus more prone to oxidative degradation (Boone, 2007; Yang, Baker, & Ward, 1992). On the other hand, the solid formulation WO_3 plus UHP could not be used in these tests. In fact, although UHP was successfully used in combination with other oxides (Bisio et al., 2016), it was found to be extremely reactive and unstable in the presence of WO_3 , as the self-decomposition of the oxidant and the *in situ* formation of large amounts water occurred immediately during the mixing of the two solid components.

The mixture WO_3 plus sodium perborate proved to be more active than the formulations containing TiO_2 plus sodium perborate, when in direct contact with CEES on the sample textile (49% vs. 27%, respectively; Figure 7(A)). However, after cleaning the contaminated area by means of a brush and removing the solid formulation, the opposite was true and a more efficient removal of the sulphide was observed with the TiO_2 plus perborate than with the WO_3 plus perborate mixture (79% vs. 64%, respectively; Figure 7(A)). This can be due to a higher specific surface area of the nanostructured titanium dioxide used in the present tests (162 $\text{m}^2 \text{g}^{-1}$ vs. 22 $\text{m}^2 \text{g}^{-1}$, for TiO_2 and WO_3 , respectively) and thus a higher adsorption capability of the contaminant by TiO_2 . Such feature played a positive role in helping the physical removal of the contaminant from the fabric sheet, thus increasing the decontamination efficiency.

On the other hand, a different behaviour was recorded in DMMP decontamination tests (Figure 7(B)). The differences between the performance of TiO_2 and WO_3 were less marked and the effect of brushing on the textile was less effective, increasing the decontamination efficiency from 19–25% to 27–32% maximum.

Higher decontamination efficiency values can be achieved by increasing the amount of solid formulation

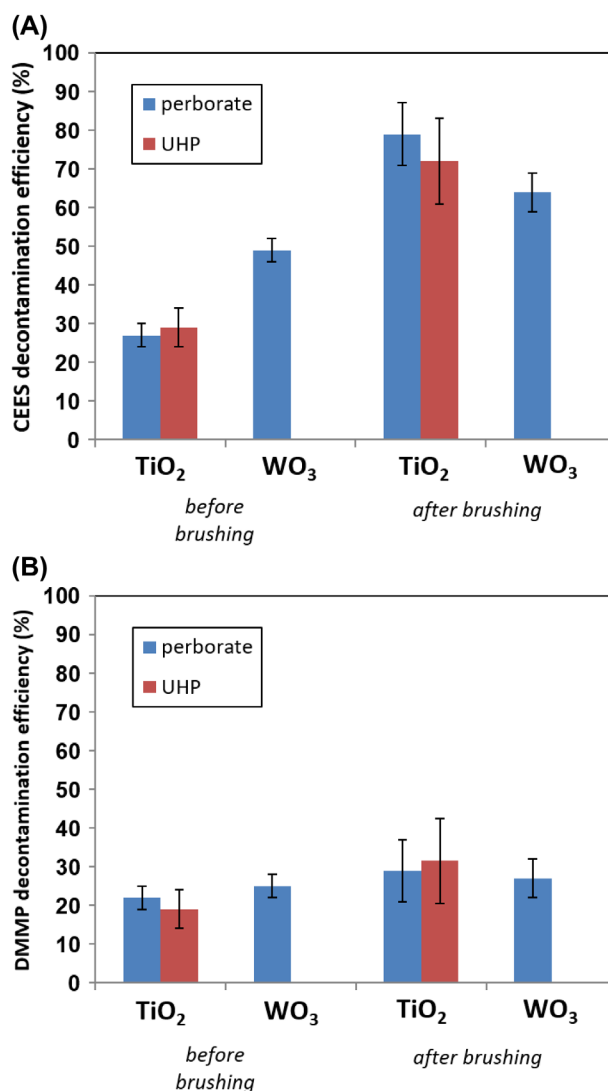


Figure 7. Oxidative decontamination of CEES (A) and DMMP (B) on cotton textile with sodium perborate tetrahydrate (blue) or urea-hydrogen peroxide adduct (red) mixed to TiO_2 or WO_3 as catalysts.

Notes: Decontamination efficiency is expressed with respect to a non-treated control (taken as 100%). Reaction conditions: 0.17 mmol CEES or DMMP (ca. 20 μL); 10 mg catalyst/oxidant mixture 1:1 wt./wt. ratio; 20 μL H_2O ; brushing after 1 min; room temperature.

(here, 10 mg of solid mixture were used on ca. 20 μL of liquid contaminant) and/or by adding larger amounts of oxidant. However, for comparative studies, these stressed reaction conditions are optimal to exalt the different catalytic properties of the various solids.

It is also worth underlining that no reports on the use of bulk tungsten trioxide for the decontamination of CWAs are present in the previous literature so far, to our best knowledge. Moreover, thanks to the presence of sodium perborate as a solid oxidant, the CWA degradation took place rapidly (within 1 min), under solvent-free conditions, with no need of UV and/or visible light irradiation and in the absence of active chlorine-containing

co-reactants. This last point is an important added value in the search for decontamination powders which do not generate chlorinated by-products that might be potentially hazardous for the human health or the environment (Boone, 2007).

In summary, both series of tests show that solid mixtures of WO_3 plus sodium perborate can potentially be used as active and efficient decontamination powders for organosulfide and organophosphonate contaminants with a performance which is, at present, fully comparable to, and sometimes better than, the one achieved over TiO_2 -containing formulations or with other catalytically active nanosized metal oxides (Štengl et al., 2005; Tang, Cheng, Zhu, Zuo, & Zhang, 2008; Winter et al., 2009; Praveen Kumar et al., 2016).

3.4. Biological impact of the catalysts

In the view of a total-loss use of the above-mentioned catalytically active powders for on-site decontamination purposes, it was thus necessary to assess their toxicological impact on the environment and living organisms. *P. leiognathi* Sh1, isolated from Azov Sea, was selected as a convenient target organism, as it is characterised by wide temperature optima (20–30 °C) and high sensitivity to various xenobiotics (van de Merwe & Leusch, 2015; Neale, Leusch, & Escher, 2017).

Targeted toxicity tests showed that neither WO_3 nor nanostructured TiO_2 affected negatively the bioluminescence of *P. leiognathi* Sh1 and hence exhibited neither acute nor chronic toxic properties (Figure 8). However, in order to understand whether tungsten-soluble species, possibly leached out or released by the parent WO_3 oxide, might have detrimental effects on bacteria, a soluble tungsten salt, namely tungsten(IV) tetrachloride, was tested as well. When WCl_4 was dissolved in water, it rapidly caused a remarkable inhibition of the bacterial bioluminescence, even at concentrations as low as 0.2 mg mL⁻¹. The inhibition effect was, conversely, partially reduced by the addition of a neutral buffer (Tris-HCl, 0.1 M, pH = 7.0), but it could not be entirely mitigated. Such behaviour suggests that part of the inhibition effect is to be attributed to the acid character developed by WCl_4 when dissolved in aqueous solutions (aqueous solutions of WCl_4 at the indicated concentrations have ca. pH 5.0). No evident negative effects on bacteria were conversely observed when tungsten centres were in solid insoluble form.

Then, the direct action of the solid catalysts on bacteria and the dependence between bacterial growth and bioluminescence were studied by additional experiments following a modification of the agar diffusion method. When WO_3 or TiO_2 was put in contact with luminescent bacteria on the surface of the agar nutrient medium, no

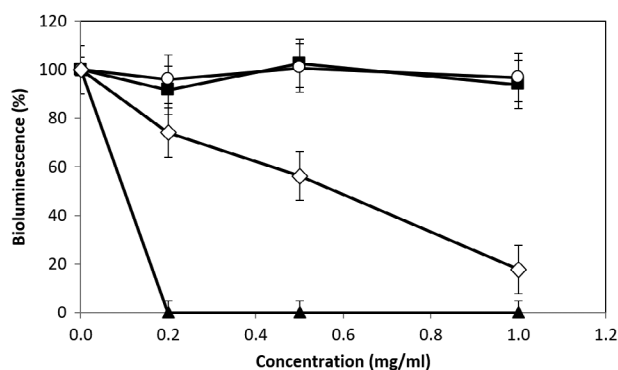


Figure 8. Typical acute and chronic effects of W- and Ti-based materials on *P. leiognathi* Sh1 bioluminescence: WO_3 (■), TiO_2 (○), WCl_4 in water (▲) and WCl_4 in buffer solution (◇).

changes were detected after 24 h of incubation. In this case, a uniform field of bacterial culture and a homogeneous emission of bioluminescence were visually observed in the daylight and in the dark, respectively. The same experiments carried out in the presence of WCl_4 , conversely, showed the formation on the agar surface of zones where both growth and bioluminescence were inhibited, at the same time (Figure S4). Thus, there is a correlation between the decrease of number of bacteria and the diminution in bioluminescence level in the presence of soluble tungsten (IV) species during the 24 h-long test. In general, these results confirm the toxic effect of the soluble forms of tungsten on *P. leiognathi* Sh1, whereas solid, insoluble WO_3 and TiO_2 phases do not give rise to any adverse biological effect on bioluminescent test bacteria.

Additional studies were performed on these samples by means of bioluminescent bioreporter *E. coli* (Lux) strains in order to assess the ability of these solid catalysts to generate mutagenic species and/or cytotoxic ROS (Chugunova et al., 2015, 2016).

In general, in these tests, the strains of *E. coli* (pSoxS-lux) and *E. coli* (pKatG-lux) are sensitive to the presence of ROS, whereas *E. coli* (pRecA-lux) and *E. coli* (pColD-lux) are sensitive to mutagenic compounds.

Solutions of aqueous H_2O_2 and dioxidine, that are inducers of luminescence, were used as positive controls and values of bioluminescence remarkably higher than 100% were thus recorded (Table 1).

The values of bacterial bioluminescence for WO_3 , WCl_4 and TiO_2 were, in all cases, lower than 100%. This means that none of the tested materials exhibited either mutagenic properties or ability to form toxic ROS.

3.5. Environmental impact of the catalysts

Finally, in order to investigate the potential impact of the most promising WO_3 catalyst onto the environment and,

in particular, on vegetable plants, the parameters of induction chlorophyll fluorescence (IChF) were studied on *P. vulgaris* L. at the stage of germination of two leaves. By monitoring IChF parameters of plant leaves it is indeed possible to detect and evaluate the presence of detrimental factors inhibiting a proper development and growth of vegetal organisms.

Bean seeds were preliminarily soaked in a suspension with different concentrations of the solid material (from 0.5 to 2.0 mg mL⁻¹). The changes on IChF curves were observed during the growth and, at the same time, the changes in the spectral characteristics of the leaf tissue of the plants were recorded (Figure S2).

After the addition of WO₃, the F_0 parameter was higher than the control. This behaviour is related to an increase in the number of inactive chlorophyll molecules, which were not able to transfer the excitation energy to the reaction centres. At the same time, the stationary level of fluorescence, F_{st} , was higher than the control and, in particular,

this value increased gradually with the concentration of WO₃ in the aqueous dispersion (Table 2). This means that the presence of the oxide had a positive effect on the transmission of photosynthetic reactions.

Another parameter that points out a non-detrimental effect of the presence of WO₃ particles on these vegetable species is $(F_p - F_{st})/F_s$, as, when it increases, it reveals a growth of the intensity of the dark fixation of CO₂. Finally, the increase in the variable fluorescence value, F_v , in the presence of WO₃, with respect to the control plant, indicates that a transition of a progressively lower number of chlorophyll molecules into an inactive form takes place.

From these observations, it can be concluded that the presence of WO₃, under these conditions, did not cause damage to the photosynthetic apparatus of the species *P. vulgaris* L.

Analogously, the effect of the presence of WO₃ was evaluated on the intensity of vigour and germination for *P. vulgaris* L. seeds. The results are summarised in Figure 9.

Table 1. Normalised values of bioluminescence intensity (%) for *E. coli* MG1655 (lux) bioreporters in the presence of TiO₂, WO₃ and WCl₄.

Sample	Concentration	Recombinant <i>E. coli</i> MG1655 bioluminescence (%)				
		pXen7	pRecA-lux	pColD-lux	pSoxS-lux	pKatG-lux
H ₂ O ₂	1.9·10 ⁻³ M	27 ± 3	150 ± 20	110 ± 21	2308 ± 190*	211 ± 6*
Dioxidine	4.4·10 ⁻⁵ M	78 ± 7	667 ± 90*	800 ± 85*	77 ± 2	100 ± 7
TiO ₂	2 mg mL ⁻¹	100 ± 5	100 ± 12	90 ± 3	77 ± 9	78 ± 9
WO ₃	2 mg mL ⁻¹	96 ± 2	93 ± 7	90 ± 3	92 ± 5	100 ± 2
WCl ₄	0.5 mg mL ⁻¹	78 ± 2	87 ± 2	80 ± 7	92 ± 5	56 ± 7

*Positive control tests.

Table 2. Effects of increasing concentrations of WO₃ sample on the induction chlorophyll fluorescence, IChF, parameters on *Phaseolus vulgaris* L. plants.

WO ₃ concentration (mg mL ⁻¹)	F_0	F_p	F_s	F_v	$(F_p - F_s)/F_s$
0.5	693.33 ± 20.80	2549.33 ± 76.48	709.33 ± 14.89	1856.00 ± 37.12	2.59 ± 0.050
1.0	629.33 ± 15.73	2512.00 ± 62.80	725.33 ± 14.51	1882.67 ± 37.65	2.46 ± 0.049
1.5	613.33 ± 12.27	2496.00 ± 62.40	730.67 ± 14.61	1882.67 ± 28.24	2.42 ± 0.048
2.0	624.00 ± 12.48	2576.00 ± 64.40	757.3 ± 15.15	1952.00 ± 29.28	2.4 ± 0.036
0 (control)	592.00 ± 8.88	2256.00 ± 33.84	704.00 ± 10.56	1664.00 ± 19.97	2.2 ± 0.026

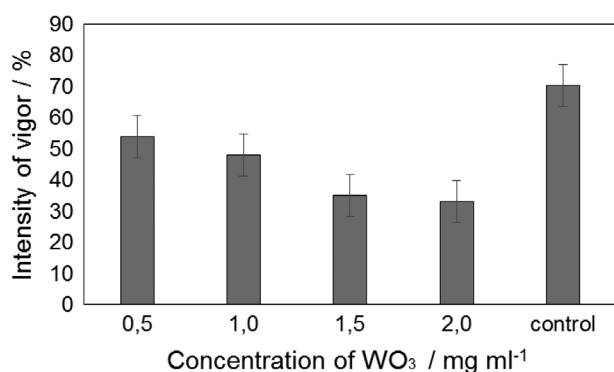


Figure 9. Effect of the concentration of WO₃ on the intensity of vigour (%) of *Phaseolus vulgaris* L seeds after 24 h. Note: Tests were replicated at least three times.

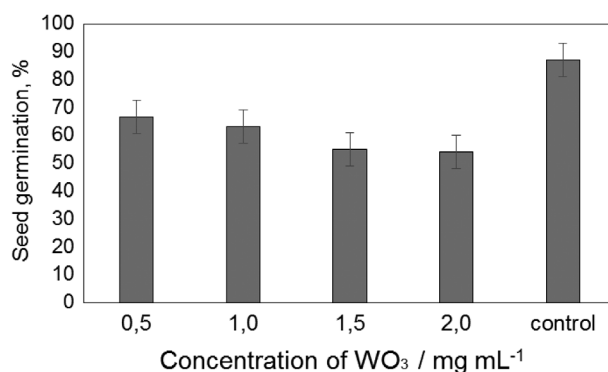


Figure 10. Effect of the concentration of WO₃ on the germination of *Phaseolus vulgaris* L seeds after 72 h. Note: Tests were replicated at least three times.

Indeed, the vigour decreased as the concentration of WO_3 increased and, in particular, the energy passed from 55% to 33% as the concentration of the solid grew from 0.5 mg mL^{-1} to 2.0 mg mL^{-1} . Since the control seeds showed an intensity of vigour of 70%, in the absence of WO_3 , the latter value approximately corresponds to the lethal dose, LD_{50} , for half of the seed population.

A similar behaviour was also found for the seed germination, which led to plants after 72 h. In this case, a similar trend was observed and the higher the concentration of WO_3 in contact with the seeds, the lower was the percentage of germinated seeds which reached the stage of plant with two leaves (Figure 10).

It is thus evident that the presence of the WO_3 sample remarkably inhibited, under the tested conditions, both the intensity of vigour and germination of *P. vulgaris* L. seeds.

4. Conclusions

A series of tests aimed at evaluating the abatement and decontamination capability of a commercially available tungsten(VI) trioxide, WO_3 , catalyst in the degradation of CWA simulants was reported in the present work for the first time.

The performance of WO_3 in the liquid-phase degradation of CEES was compared with one of a model W(IV)-heptaisobutylpolysilsesquioxane, W-POSS, that was specifically prepared and characterised in order to have a reference homogeneous catalyst with well-defined, chemically isolated and dispersed tungsten centres.

WO_3 showed a noteworthy catalytic performance in the liquid-phase oxidative abatement of CEES in the presence of aqueous hydrogen peroxide, under extremely mild conditions, if compared to nanostructured TiO_2 , which is widely considered as a reference oxide-based material for the degradation of chemical warfare agents in the presence of oxidising species.

WO_3 was then mixed in 1:1 weight ratio with sodium perborate tetrahydrate, as a chlorine-free solid oxidant, and a novel decontamination formulation for solvent-free application was obtained. Such powder proved to be active in the degradation and removal of blistering and nerve CWA simulants, within 1 min, at room temperature, from cotton textile samples. Notably, in these formulations, WO_3 showed a decontamination capability comparable to, and in some cases better than, nanostructured TiO_2 .

Finally, WO_3 did not show any acute or chronic toxicity on bioluminescent bacteria *P. leiognathi* Sh1 used as target species to evaluate the toxicological impact of the inorganic oxide materials on living micro-organisms. Conversely, in experiments carried out on the vegetable species *P. vulgaris* L. (common bean), the presence of WO_3

itself did not cause damage to the photosynthetic apparatus of the plant, whereas it inhibited markedly the energy and vigour of seed germination.

These results show that tungsten(VI) trioxide, although it has been rarely taken into account, in the recent literature, as a potential catalyst for the decontamination of chemical warfare agents, is a solid worth studying because of its promising features in terms of oxidative abatement and degradation of toxic chemicals under mild conditions, with chlorine-free oxygen-based oxidants. Nevertheless, a careful study of the potential impact of WO_3 on the environment should be further implemented. Such a cautionary approach is always advisable when a possible on-field total-loss use of catalytically active oxides is envisaged in novel formulations for CWA decontamination powders.

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