



Article

# Life Cycle Assessment of the Sustainability of Enhancing the Photodegradation Activity of TiO<sub>2</sub> with Metal-Doping

Sónia Fernandes <sup>1</sup>, Joaquim C.G. Esteves da Silva <sup>1,2</sup>  and Luís Pinto da Silva <sup>1,2,\*</sup> 

<sup>1</sup> Chemistry Research Unit (CIQUP), Faculty of Sciences of University of Porto, R. Campo Alegre 697, 4169-007 Porto, Portugal; soniaf91991@gmail.com (S.F.); jcsilva@fc.up.pt (J.C.G.E.d.S.)

<sup>2</sup> LACOMEPII, GreenUPorto, Department of Geosciences, Environmental and Territorial Planning, Faculty of Sciences of University of Porto, R. Campo Alegre 697, 4169-007 Porto, Portugal

\* Correspondence: luis.silva@fc.up.pt

Received: 10 March 2020; Accepted: 24 March 2020; Published: 25 March 2020



**Abstract:** While TiO<sub>2</sub> nanoparticles have shown potential as photocatalysts in the degradation of organic contaminants, their inability to absorb efficiently visible light has limited their industrial application. One strategy for solving this problem is monodoping TiO<sub>2</sub> photocatalysts with transition metals, which has worked in the degradation of several pollutants. However, it is not clear if this improvement is enough to offset the potential environmental impacts of adding metal ions to the synthesis of TiO<sub>2</sub>. Herein, we have used Life Cycle Assessment (LCA) to determine the sustainability of monodoping TiO<sub>2</sub> with transition metals (Fe, Co, Mn and Ni, with a 1% weight ratio) to enhance the photocatalytic properties of the photocatalyst toward the degradation of Carbamazepine and Methyl Orange, under UV-A and visible light irradiation. We found that the addition of transition-metals has no significant effect on the environmental impacts associated with the synthesis of TiO<sub>2</sub>, when a weight-based functional unit was considered. However, when photocatalytic activity was considered, major differences were found. Thus, our results demonstrate that the sustainability of monodoping with different transition metals is solely determined by their ability to enhance (or not) the photocatalytic activity of TiO<sub>2</sub>. Our data also demonstrated that isopropyl alcohol constitutes a critical point in the synthesis of TiO<sub>2</sub> photocatalysts, with ethanol being a potential substitute.

**Keywords:** life cycle assessment; TiO<sub>2</sub> photocatalysts; photodegradation; metal-doping; engineered nanomaterials

## 1. Introduction

Water pollution is an important environmental issue, as pollutants can come from different sources, e.g., pharmaceutical, pesticides, herbicides, textiles dyes, resins, and phenolic compounds, among others [1–3]. This has led to concerns regarding the depletion of underground water resources and suitable wastewater management [1].

Advanced Oxidation Processes (AOPs) constitute an innovative water treatment technology that consists of the production of highly reactive transitory species for the degradation of organic pollutants [4,5]. Heterogeneous photocatalysis employing inorganic oxides such as TiO<sub>2</sub>, ZnO, and Fe<sub>2</sub>O<sub>3</sub> has been shown to be able to efficiently degrade a broad range of pollutants without generating harmful intermediates [6]. Among them, titanium dioxide (TiO<sub>2</sub>) has received the most attention, mainly in the Research and Development (R&D) of photocatalysis technology [6].

TiO<sub>2</sub> has been commercially produced as a white pigment since the early 20th century. There is now also a market for anatase-phase TiO<sub>2</sub>, i.e., particles that fall into the nano range, with diameters between

1 and 100 nm [7]. The main advantages of TiO<sub>2</sub> photocatalyst are its low cost, chemical and thermal stability, strong oxidizing power, high photocatalytic activity, and its environmental friendliness [8]. However, the large bandgap (~3.20 eV) of TiO<sub>2</sub> means that it is only able to absorb in ultraviolet (UV) wavelengths, greatly inhibiting its industrial applications under visible-light irradiation [4,9,10]. Given this, several authors have tried to develop visible-responsive TiO<sub>2</sub> photocatalysts by doping them with either metal ions and/or nonmetal ions, or by the creation of hetero-junctions with other semiconductors [4,11,12]. Among these strategies, transition-metal doping has been shown to be quite effective [12–14].

Our group has been active in this field and has developed several TiO<sub>2</sub> nanomaterials monodoped with different metal ions, e.g., iron (Fe), cobalt (Co), manganese (Mn) and nickel (Ni) [15,16]. The photocatalytic properties of these nanoparticles were evaluated for the photo-degradation of Methyl Orange (MO) [15] and Carbamazepine (CBZ) [16] and compared with the activity shown by undoped TiO<sub>2</sub>. More specifically, undoped TiO<sub>2</sub> and monodoped Co–TiO<sub>2</sub>, Mn–TiO<sub>2</sub>, and Ni–TiO<sub>2</sub> were employed in the photo-degradation of MO under UV-A and visible light irradiation [15]. We found that while monodoping decreases the UV-A-triggered photo-degradation (from 95.6% MO conversion for undoped TiO<sub>2</sub> to 14.6–49.3% for doped nanomaterials), monodoping with Co significantly increased the photo-degradation capabilities under visible light (16.3% for undoped TiO<sub>2</sub> but 33.3% for Co–TiO<sub>2</sub>) [15]. Unfortunately, both monodoping with Mn (conversion of 6.8%) and Ni (conversion 13.8%) negatively affected the photocatalytic properties of TiO<sub>2</sub> in the degradation of MO [15].

We also tested undoped TiO<sub>2</sub> and monodoped Fe–TiO<sub>2</sub> and Co–TiO<sub>2</sub> in the UV-A and visible light-based photodegradation of CBZ [16], a persistent organic pollutant that poses a threat to water quality [14,17]. Quite encouragingly, Fe–TiO<sub>2</sub> presented better results for the removal of CBZ than undoped TiO<sub>2</sub> under both UV-A (96.9% versus 70.1%) and visible light (12.5% versus 7.9%) irradiation [16]. Moreover, while Co–TiO<sub>2</sub> presented worse results than undoped TiO<sub>2</sub> under UV-A irradiation (34.2% versus 70.1%), it also presented better results under visible light irradiation (10.8% versus 7.9%) [16].

Thus, our results also support the notion that doping TiO<sub>2</sub> with transition-metal ions is an efficient strategy to improve the visible light-based photo-degradation activity of this nanomaterial. However, it should be noted that while this appears to be a strategy with significant potential going forward, it is not clear how metal ion doping affects the sustainability of the fabrication and usage of the TiO<sub>2</sub> photocatalysts, and if the photocatalytic benefits derived from this approach can offset the potential environmental impacts. This is a glaring lack of knowledge, because if the negative environmental impacts introduced by including transition metal ions in the synthesis of TiO<sub>2</sub> photocatalysts offset the improvement of photocatalytic properties under visible light irradiation, the use of this particular doping strategy must be discouraged.

The importance of elucidating this topic is also supported by the fact that the production of nanoparticles has been shown to be more energy- and material-consuming than that of fine chemicals and pharmaceuticals [18,19]. Moreover, other studies demonstrated that the energy and chemicals used during the synthesis of nanoparticles contribute significantly to their environmental impact [20–23]. Therefore, evaluating the sustainability of the transition metal doping strategy in the synthesis and photocatalytic usage of TiO<sub>2</sub> should be a priority.

Herein, the aim of this work is to determine the sustainability of monodoping TiO<sub>2</sub> with different transition metal ions (Fe, Mn, Co, and Ni) while considering performance in the UV-A and visible light-based photo-degradation of MO and CBZ [15,16]. The sustainability and associated environmental impacts of each process were analyzed with a life cycle assessment (LCA) study of each synthesis. LCA is the most suitable approach to address this issue, as it makes it possible to quantify the environmental impacts of a given system during its life cycle [24,25]. Also, LCA has already been used with success in the environmental evaluations of different nanomaterials, such as undoped TiO<sub>2</sub> [26], silver nanoparticles [20], copper nanoparticles [21], carbon nanotubes [22], magnetic nanoparticles [23], and carbon dots [27,28].

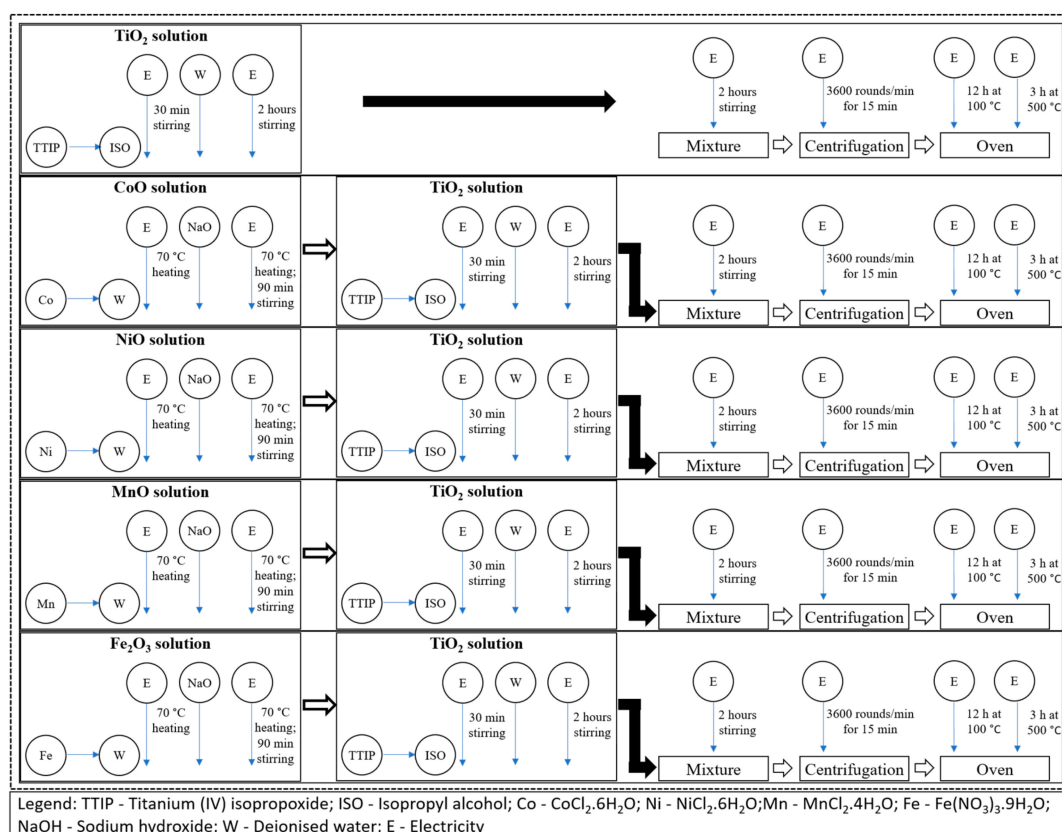
## 2. Materials and Methods

This section is divided into five subsections as described below.

### 2.1. Scope and System Boundaries

This cradle-to-grave study aims to quantify and compare the environmental impacts of undoped and transition-metal-monodoped TiO<sub>2</sub> photocatalysts in order to achieve improved pollutant degradation with reduced environmental impact. This work aims to study the laboratory-scale manufacturing stage of target nanoparticles, and considers the direct emissions from TiO<sub>2</sub> production and the indirect impacts associated with upstream resource extraction and energy generation.

This study uses the fabrication routes employed previously by us for the synthesis of undoped TiO<sub>2</sub> and monodoped Fe–TiO<sub>2</sub>, Co–TiO<sub>2</sub>, Mn–TiO<sub>2</sub>, and Ni–TiO<sub>2</sub> [13,14], which are described in detail below (Scheme 1). The environmental impacts were compared initially using a weight-based functional unit of 1 kg of nanoparticles, given that this can be used to compare the production of an equivalent amount of nanomaterial. These impacts were subsequently normalized by the photo-degradation efficiency (in %) of the photocatalysts toward the removal of either MO and CBZ under UV-A and visible light-based irradiation, as determined previously by us [15,16]. Such an approach is needed because a weight-based function might not account for the possibility that a more resource-intensive synthesis may be justified later in the use stage (given the improved functionality).



**Scheme 1.** Diagram for undoped and doped TiO<sub>2</sub> photocatalysts synthesis.

### 2.2. Synthesis Routes

The materials used in the procedure for the synthesis of all TiO<sub>2</sub> catalysts under study are detailed in the Supplementary Materials Table S1. This study considers the synthesis routes employed previously by us for the preparation of five TiO<sub>2</sub> photocatalysts, i.e., one undoped and four monodoped with transition metals (Co, Ni, Mn or Fe) [15,16]. Pure TiO<sub>2</sub> was synthesized using the sol-gel method,

and metal-doped TiO<sub>2</sub> with the sol-gel and precipitation methods combined. The amounts considered in this LCA are related to 1 kg of catalyst, and metal-doped photocatalysts constitute 1 weight percent (wt.%) of the doping elements (Co, Ni, Mn or Fe) [15,16].

Briefly, the undoped TiO<sub>2</sub> catalyst and TiO<sub>2</sub> in the doped catalysts were prepared by dissolving titanium (IV) tetraisopropoxide (TTIP) in isopropyl alcohol (ISO) under continuous stirring at room temperature for 30 min. Subsequently, water was added dropwise, and then the mixture was stirred continuously for 2 h at room temperature. The obtained dispersion was centrifuged at 3600 rpm/min for 15 min, washed with deionized water, filtered, and dried for 12 h at 100 °C in an oven. Finally, the obtained material was ground and calcined for 3 h at 500 °C [15].

For the studied metals, the dopant precursor (CoCl<sub>2</sub>, MnCl<sub>2</sub>, NiCl<sub>2</sub>, and Fe(NO<sub>3</sub>)<sub>3</sub>) was dissolved in deionized water while stirring; then, an aqueous solution of NaOH at 70 °C was added dropwise. The solutions were continuously stirred for 90 min and then the obtained solutions were added dropwise to the colloidal solutions of the TiO<sub>2</sub>, which was prepared as mentioned above. The resulting mixture was continuously stirred for 2 h and centrifuged for at 3600 rpm for 15 min. Then it was filtered, washed with deionized water, and dried in an oven for 12 h at 100 °C. The obtained nanoparticles were ground and calcined at 500 °C for 3 h [15,16].

### 2.3. Life Cycle Inventory Data

The environmental impact relative to the syntheses of TiO<sub>2</sub> photocatalysts was evaluated based on inventory data from laboratory-scale synthesis procedures found in the Ecoinvent®(Zurich, Switzerland) 3.5 database. The foreground system of the synthesis procedure consists of chemicals used as raw materials and electricity used in the fabrication process (heating plate, centrifuge, oven). The processes and chemicals included here were modeled with the following data present in the Ecoinvent®3.5 database (GLO: global; RER: regional market for Europe; and PT: Portugal):

- Isopropanol {GLO}
- Sodium hydroxide, without water, in 50% solution state {GLO};
- Cobalt {GLO};
- Nickel sulfate {GLO};
- Manganese sulfate {GLO};
- Iron (III) chloride, without water, in 40% solution state {GLO};
- Water, deionized, from tap water;
- Electricity, medium voltage {PT}.

TTIP was not included in this database, so it was introduced based on [29], as detailed in the Supporting Information on Table S2. It should be noted that while the dopant metal reagents used experimentally in the synthesis of monodoped TiO<sub>2</sub> were in the form of metal chlorides [15,16], due to the absence of these chemicals in this database, we were limited to other forms of these metal dopants (mainly metal sulfates). Our rationale for this choice was that the identity and oxidation state of the metal were expected to be more relevant for the synthesis of metal-doped TiO<sub>2</sub>, and not the identity of the anionic nonmetal compounds of the metal precursor.

The amount of chemicals and electricity used are described in Section 2.2 and in the Supplementary Materials. The dataset used for electricity describes the available electricity data on the medium voltage level in Portugal for the year 2014, as described in the Ecoinvent®3.5 database. The electricity consumption considered here is what is required to use the heating plate, oven, and centrifuge. The heating and stirring were done using a Normax Nx1200 Analogical magnetic stirrer (Marinha Grande, Portugal) with heating, which has a power consumption of 500 W. Centrifugation was done with a Hettich MIKRO 220R (Tuttlingen, Germany) with 3.8 A and a maximum power consumption of 874 W with a maximum power factor (1). The oven used was a Furnace 47900 from Thermolyne, which has a power consumption of 1000 W.

#### 2.4. Environmental Impact Assessment

The present LCA study is based on a cradle-to-grave approach, i.e., from the production of precursor materials to their disposal. Environmental impact was modeled using the ReCiPe 2016 V1.03 endpoint method, Hierarchist version, [30], which evaluates three categories of potential impacts (Human Health, Ecosystems, and Resources). In the Human Health subsection, Global Warming–Human Health (GW–HH), Stratospheric ozone depletion (SO), Ionization Radiation (IR), Ozone formation–Human Health (OF–HH), Fine Particulate Matter formation (FPM), Human Carcinogenic toxicity (HC), Human Non-Carcinogenic toxicity (HNC) and Water Consumption–Human Health (WC–HH). Ecosystems potential impacts evaluated Global Warming–Terrestrial Ecosystems (GW–TE), Global Warming–Freshwater Ecosystems (GW–FE), Ozone Formation–Terrestrial Ecosystems (OF–TE), Terrestrial acidification (TA), Freshwater Eutrophication (FE), Marine Eutrophication (ME), Terrestrial EcoToxicity (TET), Freshwater EcoToxicity (FET), Marine EcoToxicity (MET), Land Use (LU), Water Consumption–Terrestrial Ecosystem (WC–TE) and Water Consumption–Aquatic Ecosystems (WC–AE) were assessed. In the Resources subsection, Mineral Resource scarcity (MR) and Fossil Resource scarcity (FR) were assessed. The LCA study was performed using SimaPro 9.0.0.48 software (Amersfoort, The Netherlands).

#### 2.5. Sensitivity Analysis

Given that doped TiO<sub>2</sub> photocatalysts are in the early stages of development on a laboratory scale, the environmental impact of their fabrication is still uncertain. To this end, a sensitivity analysis was performed in order to reduce such uncertainties for scaled-up production [31]. This was done by considering “what-if” scenarios [32], that is, by changing the amount and type of materials and electricity employed in the synthesis of these photocatalysts.

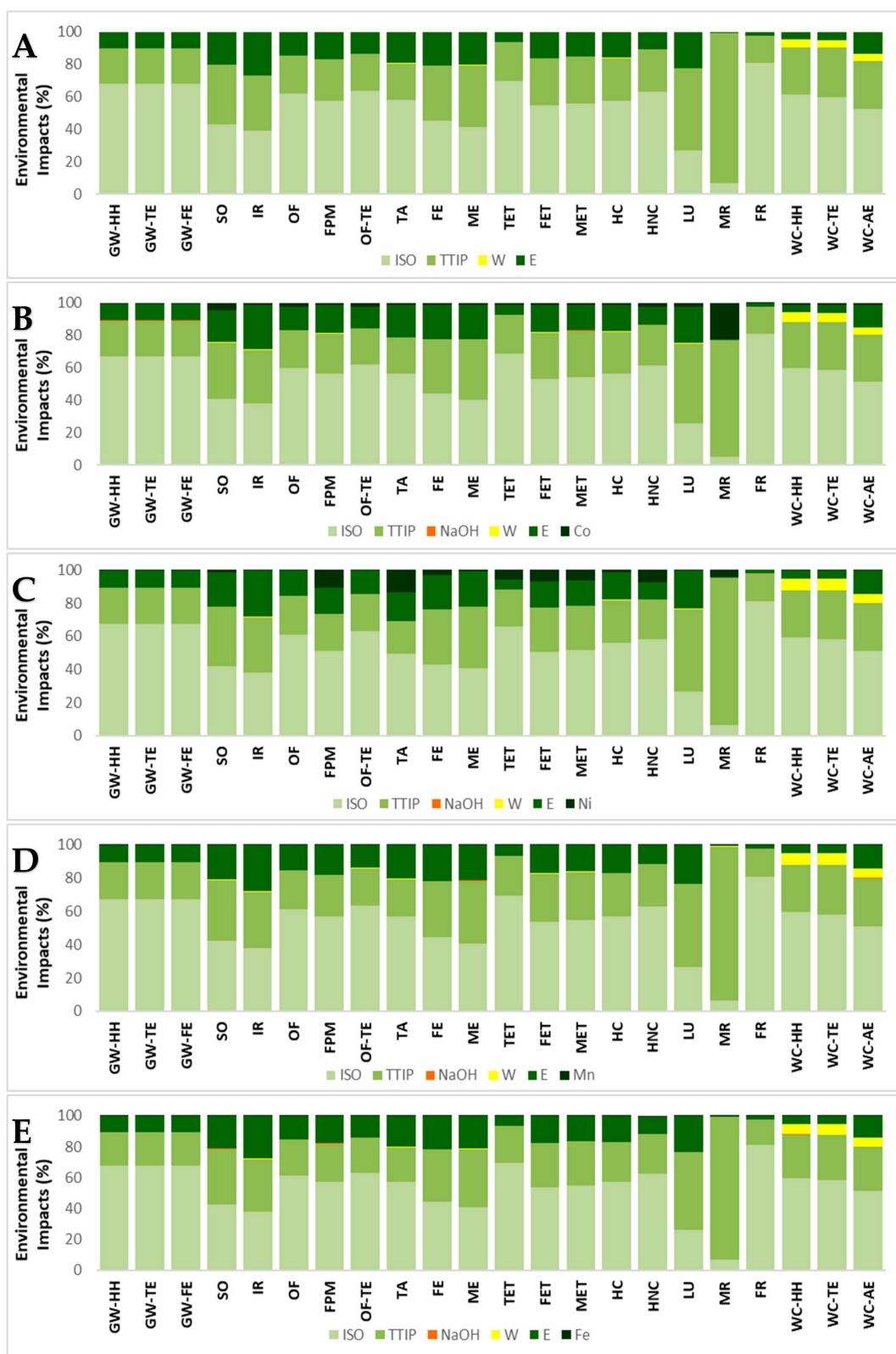
### 3. Results

#### 3.1. Synthesis Comparison by Weight

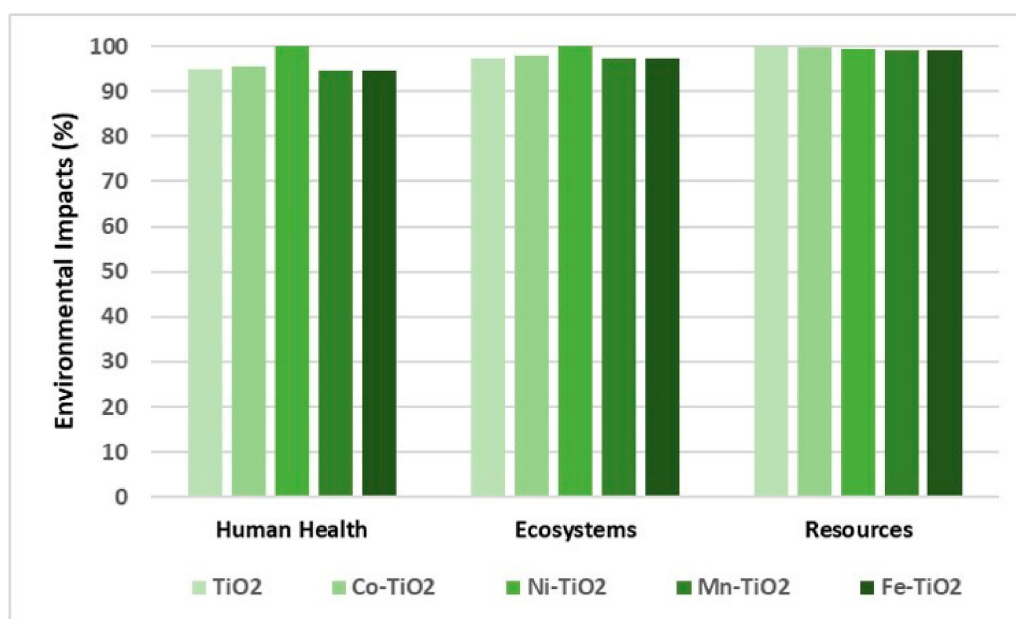
The potential environmental impacts of the undoped and metal-doped TiO<sub>2</sub> catalysts under study are shown in Figure 1. From this analysis, it was possible to see that the major contributor in almost all the environmental impact categories is ISO. The categories of Land Use (LU) and Mineral Resource Scarcity (MR) are the exceptions, in which TTIP is the highest contributor. Deionized water appears to be a comparatively negligible contributor, even in impact categories related to water consumption. These results are in line with the literature; a recent work by Wu et al. [33] demonstrated that different precursors have the greatest environmental impact for chemical synthesis routes, such as the sol-gel approach studied here [15,16].

Interestingly, no significant differences appear to exist between the syntheses of undoped and monodoped TiO<sub>2</sub> photocatalysts (Figure 1). In fact, only the addition of Co and Ni precursors leads to some differences regarding the resulting environmental impact, namely, the Co precursor is the second major contributor concerning Mineral Resource Scarcity (MR), while the addition of nickel precursors implies a slight contribution from this material for Fine Particulate Matter formation (FPM) and Terrestrial Acidification (TA). Thus, our results indicate that the addition of doping metals does not significantly affect the sustainability of TiO<sub>2</sub> fabrication.

This was confirmed by comparing the environmental impacts associated with the five nanomaterials, as presented in Figure 2. The differences are negligible in the Resources category, and quite low in the Human Health and Ecosystem categories. In fact, for the latter two categories, only Ni–TiO<sub>2</sub> induces slightly higher impacts, while the other four nanoparticles present identical impacts. Nevertheless, the small differences between Ni–TiO<sub>2</sub> and the other nanoparticles are probably not significant.



**Figure 1.** Relative environmental impacts of synthesis of the undoped TiO<sub>2</sub> photocatalyst (A), Co-doped TiO<sub>2</sub> photocatalyst (B), Ni-doped TiO<sub>2</sub> photocatalyst (C), Mn-doped TiO<sub>2</sub> photocatalyst (D), and Fe-doped TiO<sub>2</sub> photocatalyst (E).



**Figure 2.** Relative environmental impact of different TiO<sub>2</sub> photocatalysts, considering a weight-functional unit of 1 kg.

### 3.2. Synthesis Comparison by Photocatalytic Activity

The environmental profiles (Figure 3) were also evaluated for the synthetic routes of the different TiO<sub>2</sub> photocatalysts according to their photocatalytic activity in the degradation of either CBZ or MO, both under UV-A and visible light irradiation (Table 1).

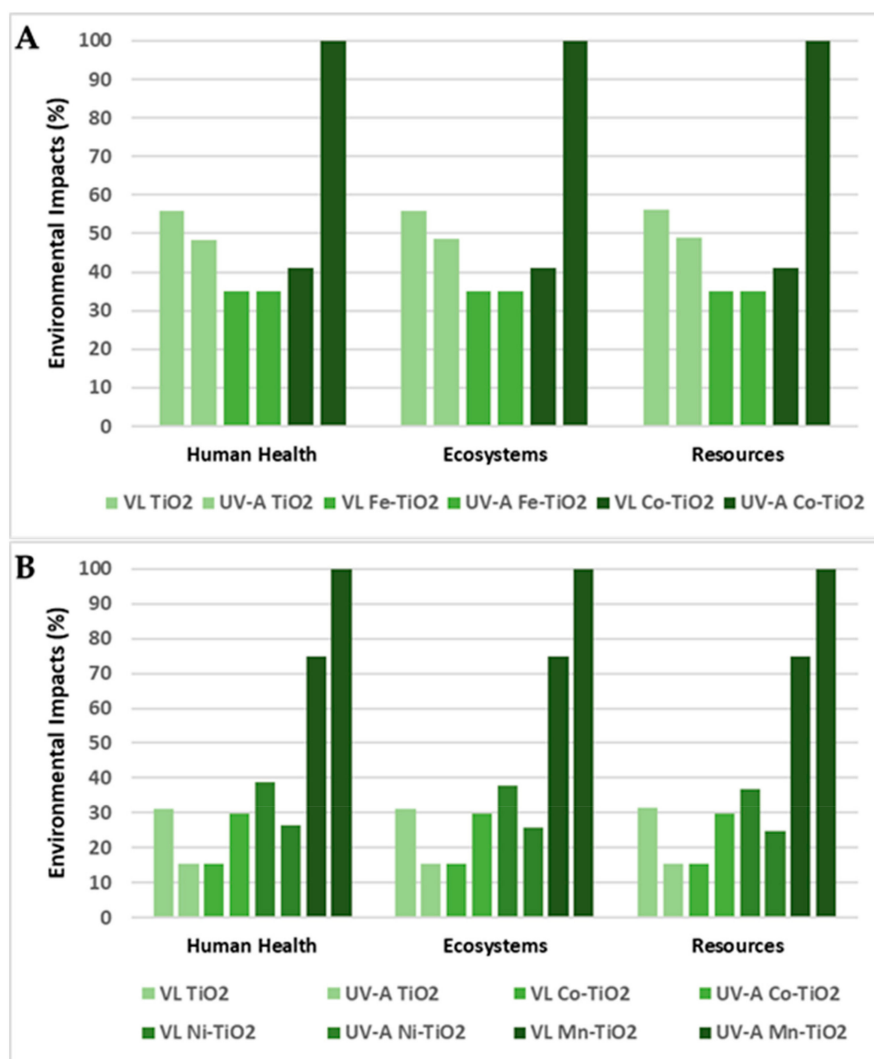
**Table 1.** Functional unit based on photocatalytic activity for each pollutant under study. “-” refers to cases in which the photocatalysts were not used.

Photocatalyst	CBZ		MO	
	VL	UV-A	VL	UV-A
Fe-TiO <sub>2</sub>	1.00	1.00	-	-
Undoped TiO <sub>2</sub>	1.59	1.38	2.04	1.00
Co-TiO <sub>2</sub>	1.16	2.83	1.00	1.94
Ni-TiO <sub>2</sub>	-	-	2.41	1.63
Mn-TiO <sub>2</sub>	-	-	4.90	6.55

The rescaling was done by considering the photo-degradation of each pollutant under each type of light source, i.e., the function-based functional unit is presented as a ratio,  $\frac{\text{Photocatalytic activity}_{NP}^{REF}}{\text{Photocatalytic activity}_{NP}}$ , in which the photocatalytic activity of each nanoparticle (NP) consists of the removal efficiency (in %) of the target pollutant as determined previously [15,16], while  $\text{Photocatalytic activity}_{NP}^{REF}$  refers to the nanoparticles with higher photocatalytic activity for each case (thus acting as a reference). Therefore, higher functional units indicate lower photocatalytic activity and higher associated environmental impact.

For CBZ (Figure 3A), significant differences exist according to the function-based functional unit, which illustrates the importance of considering the photocatalytic activity of CBZ degradation. More specifically, there is little difference for the weight-based functional unit (Figure 2). However, for the functional unit based on photocatalytic activity, Co-TiO<sub>2</sub> clearly leads to greater potential impacts than both Fe-TiO<sub>2</sub> and undoped TiO<sub>2</sub>, under both UV-A and visible light irradiation. Interestingly, Fe-TiO<sub>2</sub> has a lower environmental impact than undoped TiO<sub>2</sub> under both types of light sources, which can be explained by the higher photocatalytic activity of the former nanomaterial. Thus, our analysis

demonstrates that Fe monodoping is a sustainable strategy for improving the photocatalytic activity of TiO<sub>2</sub> in the degradation of CBZ.



**Figure 3.** Relative environmental impacts of different TiO<sub>2</sub> photocatalysts synthesis for CBZ (A) and MO (B), considering photocatalytic activity as a functional unit, under either UV-A or visible-light (VL) irradiation.

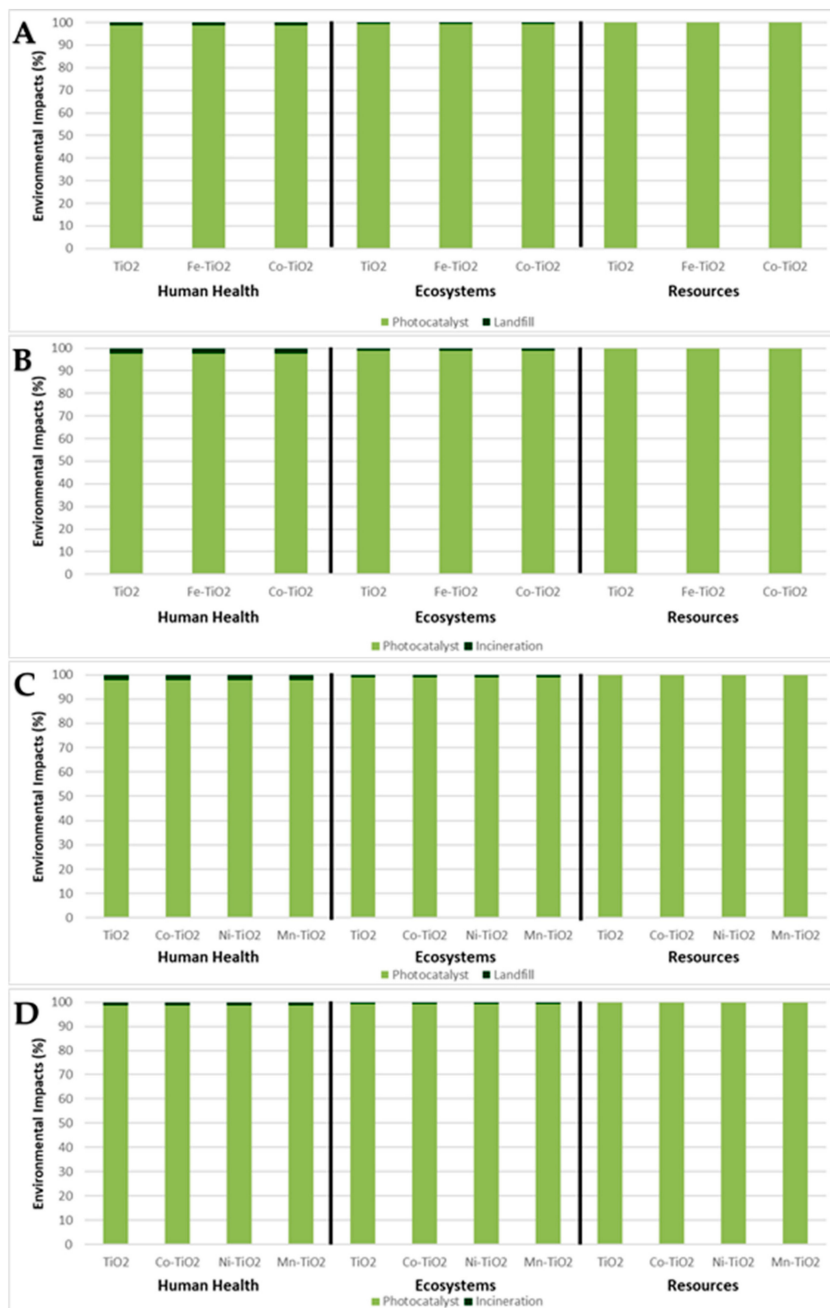
For MO (Figure 3B), Co-TiO<sub>2</sub> is the nanoparticle with the lowest environmental impact under visible light, while undoped TiO<sub>2</sub> was associated with lower impacts for UV-A-based photo-degradation. For both visible and UV-A light, Mn-TiO<sub>2</sub> leads to greater potential environmental impacts. Thus, we can conclude that for MO degradation, Mn- and Ni-doping are poor choices under both UV-A and visible light irradiation. As for Co-doping, it is indeed a sustainable approach for the photo-degradation of MO under visible light. However, undoped TiO<sub>2</sub> is still the best choice under UV-A irradiation.

Our results indicate that the identity of the photocatalyst associated with greater environmental impacts changes with the employed functional unit. In this sense, Ni-TiO<sub>2</sub> has a greater potential impact on human health and ecosystems, while undoped TiO<sub>2</sub> has a greater impact in terms of resources when a weight-based functional unit is considered. When the LCA study considered the photocatalytic activity of the nanomaterial, Mn-TiO<sub>2</sub> was found to be the catalyst with worst environmental performance among all the categories and under both visible and UV-A light.

In order to better understand the life cycle, two possibilities for the disposal scenario were evaluated: Landfill and Incineration (Figure 4). For both CBZ (Figure 4A,B) and MO (Figure 4C,D),



incineration has a slightly greater impact than landfill disposal. However, the contribution of both landfill and incineration is quite small when compared with the synthesis stage. Therefore, it is possible to conclude that the catalyst synthesis stage represents the key part of the life cycle in terms of potential environmental impact.



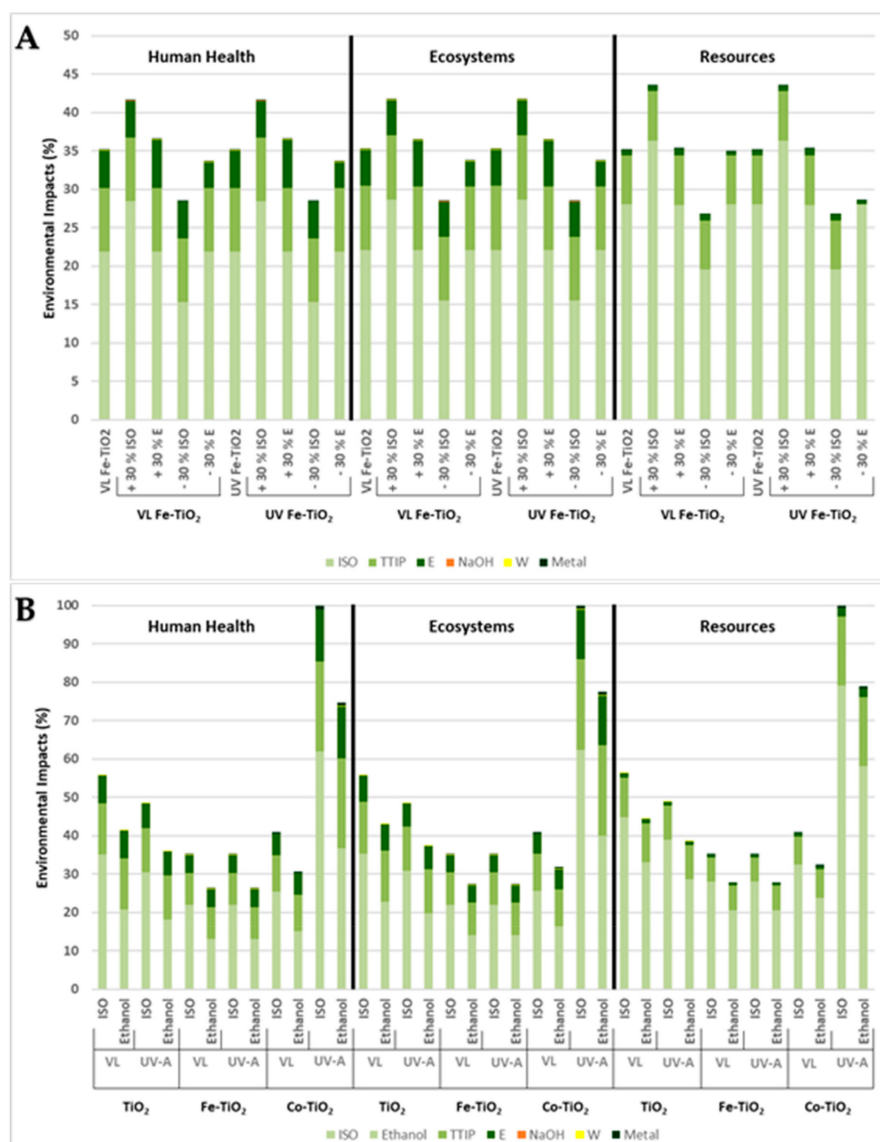
**Figure 4.** Relative environmental impacts of different TiO<sub>2</sub> photocatalysts synthesis for CBZ degradation considering disposal in Landfill (A) or Incineration (B), as well for MO degradation according to Landfill (C) and Incineration (D) disposal.

### 3.3. Sensitivity Analysis

A sensitivity analysis was performed for both CBZ and MO degradation. This analysis varied both the amount ( $\pm 30\%$ ) of electricity and the raw material associated with most impacts (ISO). This was done for the photocatalysts with lower potential environmental impacts in the degradation of the

organic contaminants. The substitution of the material with the greatest impact for another that can serve in the synthesis of these catalysts was also evaluated.

For CBZ degradation, the Fe–TiO<sub>2</sub> photocatalyst has the lowest environmental impact in visible and UV-A light, which motivated the sensitivity analysis regarding this catalyst (Figure 5A). In this sense, changing the amount of ISO has a significant effect on the human health ( $\pm 7\%$ ), ecosystems ( $\pm 7\%$ ), and resources ( $\pm 8\%$ ) categories. On the other hand, varying the electricity (E) has a negligible effect on human health (i.e., an increase of 1% and a decrease of 2%), ecosystems ( $\pm 1\%$ ), and an even lower effect on resources ( $\pm 0.2\%$ ) impacts.

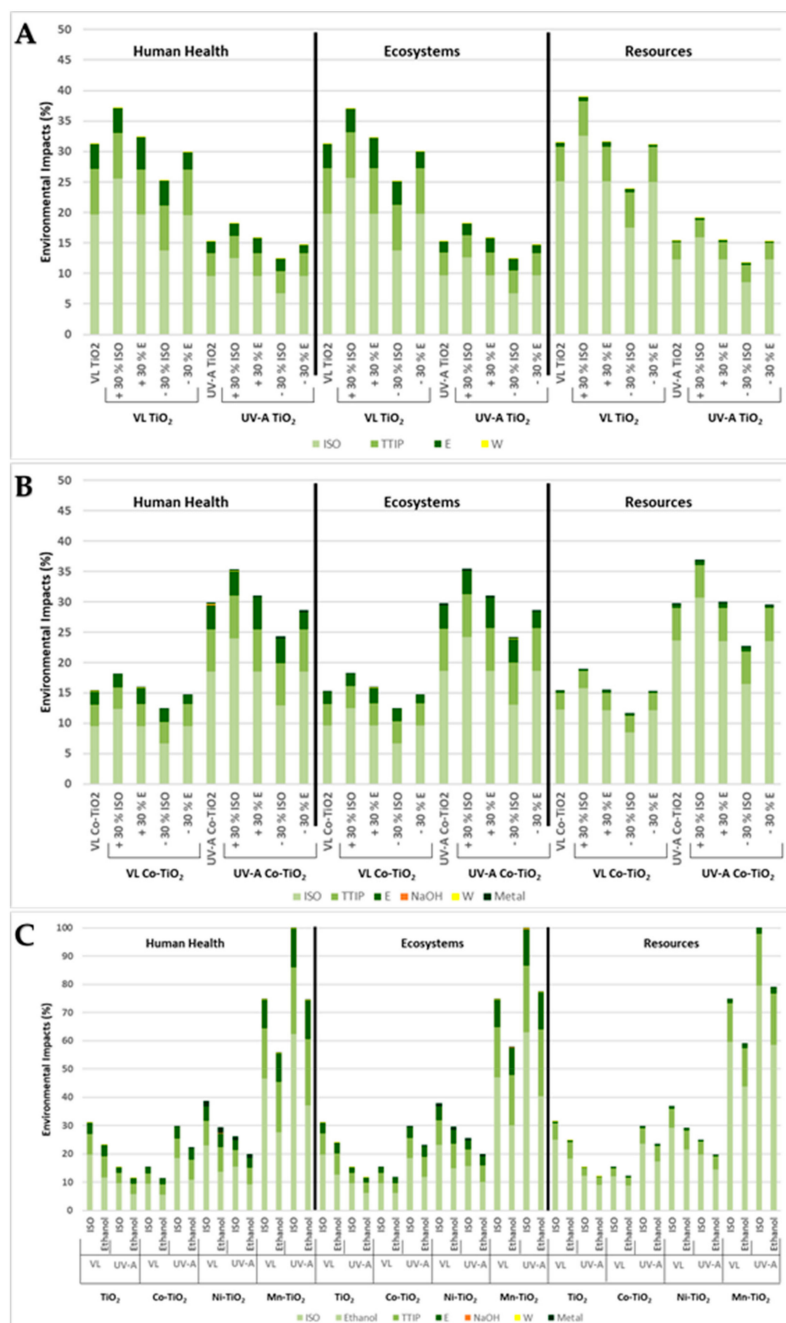


**Figure 5.** Relative environmental impacts for sensitivity analysis of Fe–TiO<sub>2</sub> photocatalyst (A) and comparison of the substitution of ISO with Ethanol (B) in CBZ degradation, under either UV-A or visible-light (VL) irradiation.

As observed, ISO is the reagent with the greatest potential environmental impact. As such, a sensitivity analysis was also performed by substituting this compound for another that has been considered in the literature for the synthesis of TiO<sub>2</sub> photocatalysts, namely, ethanol [34]. The results of replacing ISO with ethanol are shown in Figure 5B. Our data indicated that, among all the photocatalysts, the use of ethanol implies less potential environmental impact in all the categories. Beyond this, a higher decrease was observed for Co–TiO<sub>2</sub> under UV-A light, which presented differences higher than

20%. In fact, it has already been observed that changing the organic solvent can modify the resulting environmental impact; Wu et al. [33] found that using 1-butanol as an organic solvent has a greater environmental impact than using ISO.

For MO degradation, the photocatalyst with best performance was TiO<sub>2</sub> doped with Co under visible light, and the undoped catalyst under UV-A light (Figure 6).



**Figure 6.** Relative environmental impact for sensitivity analysis of undoped (A), Co-TiO<sub>2</sub> (B) photocatalyst and comparison of the substitution of ISO with Ethanol (C) in MO degradation, under either UV-A or visible-light (VL) irradiation.

The results for the Co-TiO<sub>2</sub> catalyst are presented in Figure 6A. When we changed the amount of ISO, we observed (under visible light) moderate effects on the human health and ecosystems ( $\pm 3\%$ ) categories, and a slightly higher effect on resources ( $\pm 4\%$ ). The same changes, but under UV-A light, had substantial influences on the human health, ecosystems (for both categories differences of  $\pm 6\%$ ),

and resources ( $\pm 8\%$ ) categories. The effects of varying the electricity (under both visible and UV-A light) were insignificant for human health, ecosystems with  $\pm 1\%$ , as well as for resources, with  $\pm 0.1\%$  (VL) and  $0.2\%$  (UV-A).

The results of the sensitivity analysis of the undoped  $\text{TiO}_2$  photocatalyst are shown in Figure 6B, in which the opposite behavior of Co- $\text{TiO}_2$  was observed. More specifically, changing the amount of ISO under visible light has substantial effects on the human health, ecosystems, and resources categories ( $\pm 6\%$ ,  $\pm 6\%$  and  $\pm 8\%$ , respectively). Under UV-A light, a moderate influence on the human health ( $\pm 3\%$ ), ecosystems ( $\pm 3\%$ ), and resources ( $\pm 4\%$ ) categories was observed. Changing the amount of electricity still leads to insignificant effects for all categories.

The effect of replacing ISO with ethanol (Figure 6C) was also evaluated. This led to lower potential environmental impacts in all the categories, which were higher for Mn- $\text{TiO}_2$  with differences greater than 15% under visible light and above 20% under UV-A light. Replacing ISO with ethanol does not change the photocatalysts with better performance relative to their environmental impact (visible light: Co- $\text{TiO}_2$ ; UV-A: undoped  $\text{TiO}_2$ ).

#### 4. Conclusions

This study applies a first Life Cycle Assessment (LCA) to  $\text{TiO}_2$  photocatalysts synthesis with the purpose of evaluating the environmental performance of transition-metal-monodoped catalysts in the degradation of specific organic contaminants, Carbamazepine and Methyl Orange (respectively, a pharmaceutical and water contaminant).

Our LCA study revealed that transition-metal-monodoping has a limited environmental impact on the synthesis of  $\text{TiO}_2$  photocatalysts when considering a weight-based functional unit (1 kg). However, when the photocatalytic activity of each nanomaterial was taken into account, major differences were found. Thus, our results demonstrate that the comparative sustainability of monodoping with different transition metals is solely determined by their ability to enhance (or not) the photocatalytic activity of  $\text{TiO}_2$ .

Our LCA approach also revealed that isopropyl alcohol is the reagent that has by far the highest environmental impact, with the exception of the Land Use and Mineral Resource Scarcity categories, in which the titanium precursor is the highest contributor. A sensitivity analysis indicated that varying the amount of isopropyl alcohol ( $\pm 30\%$ ) leads to important changes in the environmental profiles of the studied  $\text{TiO}_2$  photocatalysts. These results imply that isopropyl alcohol constitutes a critical point in the synthesis, and it should be focused on in studies aiming to increase the sustainability of producing  $\text{TiO}_2$  photocatalysts. Our results also indicated that replacing this chemical with ethanol increases the sustainability of these processes; therefore, further studies should be made to assess the implications of this change in the photocatalytic performance of this type of nanomaterial.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/1996-1944/13/7/1487/s1>, Table S1. Amount of materials used in this LCA for each photocatalyst; Table S2. Inputs introduced in Ecoinvent database to achieve titanium precursor.

**Author Contributions:** Conceptualization: L.P.d.S.; Investigation: S.F. and L.P.d.S.; writing—Original draft preparation: S.F. and L.P.d.S.; writing—Review and editing: L.P.d.S. and J.C.G.E.d.S.; supervision: L.P.d.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was made in the framework of project UIDB/00081/2020, funded by the Portuguese “Fundação para a Ciência e Tecnologia” (FCT, Lisbon). Luís Pinto da Silva also acknowledges funding from FCT under the Scientific Employment Stimulus (CEECIND/01425/2017).

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Gnanasekaran, L.; Hemamalini, R.; Saravanan, R.; Ravichandran, K.; Gracia, F.; Gupta, V. Intermediate state created by dopant ions (Mn, Co and Zr) into  $\text{TiO}_2$  nanoparticles for degradation of dyes under visible light. *J. Mol. Liq.* **2016**, *223*, 652–659. [[CrossRef](#)]

2. Rizzi, V.; Prasetyanto, E.A.; Chen, P.; Gubitosa, J.; Fini, P.; Agostiano, A.; De Cola, L.; Cosma, P. Amino grafted MCM-41 as highly efficient and reversible ecofriendly adsorbent material for the Direct Blue removal from wastewater. *J. Mol. Liq.* **2019**, *273*, 435–446. [[CrossRef](#)]
3. Rizzi, V.; Romanazzi, F.; Gubitosa, J.; Fini, P.; Romita, R.; Agostiano, A.; Petrella, A.; Cosma, P. Chitosan Film as Eco-Friendly and Recyclable Bio-Adsorbent to Remove/Recover Diclofenac, Ketoprofen, and Their Mixture from Wastewater. *Biomolecules* **2019**, *9*, 571. [[CrossRef](#)] [[PubMed](#)]
4. El Mragui, A.; Daou, I.; Zegaoui, O. Influence of the preparation method and ZnO/(ZnO + TiO<sub>2</sub>) weight ratio on the physicochemical and photocatalytic properties of ZnO-TiO<sub>2</sub> nanomaterials. *Catal. Today* **2018**, *312–322*, 41–51. [[CrossRef](#)]
5. El Mragui, A.; Zegaoui, O.; Daou, I. Synthesis, characterization and photocatalytic properties under visible light of doped and co-doped TiO<sub>2</sub>-based nanoparticles. *Mater. Today: Proc.* **2019**, *13*, 857–865. [[CrossRef](#)]
6. Chong, M.N.; Jin, B.; Chow, C.W.K.; Saint, C. Recent developments in photocatalytic water treatment technology: A review. *Water Res.* **2010**, *44*, 2997–3027. [[CrossRef](#)]
7. Grubb, G.F.; Bakshi, B.R. Life Cycle of Titanium Dioxide Nanoparticle Production, Impact of Emissions and Use of Resources. *J. Ind. Ecol.* **2010**, *15*, 81–95. [[CrossRef](#)]
8. Joshi, M.M.; Labhsetwar, N.K.; Mangrulkar, P.A.; Tijare, S.N.; Kamble, S.P.; Rayalu, S.S. Visible light induced photoreduction of methyl orange by N-doped mesoporous titania. *Appl. Catal. A* **2009**, *357*, 26–33. [[CrossRef](#)]
9. D'Amato, C.A.; Giovannetti, R.; Zannotti, M.; Rommozzi, E.; Minicucci, M.; Gunnella, R.; Di Cicco, A. Band Gap implications on Nano-TiO<sub>2</sub> surface modification with ascorbic acid for visible light-active polypropylene coated photocatalyst. *Nanomaterials* **2018**, *8*, 599–613. [[CrossRef](#)]
10. Liu, J.; Li, Y.; Ke, J.; Wang, S.; Wang, L.; Xiao, H. Black NiO-TiO<sub>2</sub> nanorods for sola photocatalysis: Recognition of electronic structure and reaction mechanism. *Appl. Catal. B* **2018**, *224*, 705–714. [[CrossRef](#)]
11. Cheng, J.; Qiu, F.; Xu, W.; Cao, S.; Zhu, H. Recent progress in enhancing photocatalytic efficiency of TiO<sub>2</sub>-based materials. *Appl. Catal. A* **2015**, *495*, 131–140. [[CrossRef](#)]
12. Wang, E.; Yang, W.; Cao, Y. Unique surface chemical species on Indium doped TiO<sub>2</sub> and their effect on the visible light photocatalytic activity. *J. Phys. Chem. C* **2009**, *113*, 20912–20917. [[CrossRef](#)]
13. Lv, T.; Zhao, J.; Chen, M.; Shen, K.; Zhang, D.; Zhang, J.; Zhang, G.; Liu, Q.; Cao, Y. Boosted visible-light photodegradation of methylene blue by V and Co Co-doped TiO<sub>2</sub>. *Materials* **2018**, *11*, 1946–1958. [[CrossRef](#)]
14. Ma, X.; Zhou, W.; Chen, Y. Structure and photocatalytic properties of Mn-doped TiO<sub>2</sub> loaded on wood-based activated carbon fiber composites. *Materials* **2017**, *10*, 631–641.
15. El Mragui, A.; Zegaoui, O.; Daou, I.; Esteves da Silva, J.C.G. Preparation, characterization, and photocatalytic activity under UV and visible light of Co, Mn, and Ni mono-doped and (P,Mo) and (P,W) co-doped TiO<sub>2</sub> nanoparticles: A comparative study. *Environ. Sci. Pollut. Res.* **2019**, 1–16. [[CrossRef](#)] [[PubMed](#)]
16. El Mragui, A.; Logvina, Y.; Pinto da Silva, L.; Zegaoui, O.; Esteves da Silva, J.C.G. Synthesis of Fe- and Co-Doped TiO<sub>2</sub> with Improved Photocatalytic Activity Under Visible Irradiation Toward Carbamazepine Degradation. *Materials* **2019**, *12*, 3874–3888. [[CrossRef](#)]
17. Jaria, G.; Silva, C.P.; Oliveira, J.A.B.P.; Santos, S.M.; Gil, M.V.; Otero, M.; Calisto, V.; Estves, V.I. Production of highly efficient activated carbons from industrial wastes for the removal of pharmaceuticals from water—A full factorial design. *J. Hazard. Mater.* **2019**, *370*, 212–218. [[CrossRef](#)] [[PubMed](#)]
18. Eckelman, M.J.; Zimmerman, J.B.; Anastas, P.T. Toward Green Nano, E-factor analysis of several nanomaterial syntheses. *J. Ind. Ecol.* **2008**, *12*, 316–328.
19. Pourzahedi, L.; Eckelman, M.J. Comparative life cycle assessment of silver nanoparticle synthesis routes. *Environ. Sci.* **2015**, *2*, 361–369. [[CrossRef](#)]
20. Bafana, A.; Kumar, S.V.; Temizel-Sekeryan, S.; Dahoumane, S.A.; Haselbach, L.; Jeffryes, C.S. Evaluating microwave-synthesized silver nanoparticles from silver nitrate with life cycle assessment techniques. *Sci. Total Environ.* **2018**, *636*, 936–943. [[CrossRef](#)]
21. Yubing, P.; Feng, T.; Adam, P.; Laratte, B.; Ionescu, R.E. Fate and characterization factors of nanoparticles in seventeen subcontinental freshwaters: A case study on copper nanoparticles. *Environ. Sci. Technol.* **2016**, *50*, 9370–9379.
22. Upadhyayula, V.K.K.; Meyer, D.E.; Curran, M.A.; Gonzalez, M.A. Life cycle assessment as a tool to enhance the environmental performance of carbon nanotube products: A review. *J. Clean. Prod.* **2012**, *26*, 37–47. [[CrossRef](#)]

23. Feijoo, S.; González-García, S.; Moldes-Diz, Y.; Vazquez-Vasquez, C.; Feijoo, G.; Moreira, M.T. Comparative life cycle assessment of diferente synthesis routes of magnetic nanoparticles. *J. Clean. Prod.* **2017**, *143*, 528–538. [[CrossRef](#)]
24. Ramos, A.; Teixeira, C.A.; Rouboa, A. Assessment study of an advanced gasification strategy at low temperature for syngas generation. *Int. J. Hydrog. Energy* **2018**, *43*, 10155–10166. [[CrossRef](#)]
25. Ramos, A.; Teixeira, C.A.; Rouboa, A. Environmental analysis of waste-to-energy—A portuguese case study. *Energies* **2018**, *11*, 548–574. [[CrossRef](#)]
26. Pini, M.; González, E.I.C.; Neri, P.; Siligardi, C.; Ferrari, A.M. Assessment of Environmental Performance of TiO<sub>2</sub> Nanoparticles Coated Self-Cleaning Float Glass. *Coatings* **2017**, *7*, 8. [[CrossRef](#)]
27. Christé, S.; Esteves da Silva, J.C.G.; Pinto da Silva, L. Evaluation of the environmental impact and efficiency of N-doping strategies in the synthesis of carbon dots. *Materials* **2020**, *13*, 504–518. [[CrossRef](#)]
28. Sendão, R.; Martínez de Yuso, M.; Algarra, M.; Esteves da Silva, J.C.G.; Pinto da Silva, L. Comparative life cycle assessment of bottom-up synthesis routes for carbon dots derived from citric acid and urea. *J. Clean. Prod.* **2020**, *254*, 120080–120090. [[CrossRef](#)]
29. Tsang, M.; Philippot, G.; Aymonier, C.; Sonnemann, G. Anticipatory Life-cycle assessment of supercritical fluid synthesis of barium strontium titanate nanoparticles. *Electron. Suppl. Mater. (Esi) Green Chem.* **2016**, *18*, 4924–4933. [[CrossRef](#)]
30. Huijbregts, M.A.J.; Steinmann, Z.J.N.; Elshout, P.M.F.; Stam, G.; Verones, F.; Vieira, M.; Zijp, M.; Hollander, A.; Zelm, R. ReCiPe2016: A harmonized life cycle impact assessment method at midpoint and endpoint level. *Int. J. Life Cycle. Assess.* **2017**, *22*, 138–147. [[CrossRef](#)]
31. Kazemi, A.; Bahramifar, N.; Heydari, A.; Olsen, S.I. Life cycle assessment of nanoadsorbents at early stage technological development. *J. Clean. Prod.* **2018**, *174*, 527–537. [[CrossRef](#)]
32. Pianosi, F.; Beven, K.; Freer, J.; Hall, J.W.; Rougier, J.; Stephenson, D.B.; Wagener, T. Sensitivity analysis of environmental models: A systematic review with practical workflow. *Environ. Model. Softw.* **2016**, *79*, 214–232. [[CrossRef](#)]
33. Wu, F.; Zhou, Z.; Hicks, A.L. Life Cycle Impact of Titanium Dioxide Nanoparticles Synthesis through Physical, Chemical, and Biological Routes. *Environ. Sci. Technol.* **2019**, *53*, 4078–4087. [[CrossRef](#)]
34. Khalid, N.R.; Majid, A.; Tahir, M.; Niaz, N.A.; Khalid, S. Carbonaceous-TiO<sub>2</sub> nanomaterials for photocatalytic degradation of pollutants: A review. *Ceram. Int.* **2017**, *43*, 14552–14571. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).