Uberlândia, September 28, 2020.

Dear Editor,

Firstly, we hope you and your family are well.

We are submitting a revised version of our article in which some suggestions and/or comments made have been incorporated or considered. The added changes were marked in yellow. Corrected figures (Figure 2, Figure S1, Figure S5a and S5b) and Tables 1 to 3 are being sent in substitution.

Finally, we did, in the best way we could, the additional adjustments recommended after the analysis made by you and the two Referee. As for dismembering, at this point, the section containing the results together with the discussion in a section only for results and another containing only the discussions, will not be an easy task, and it is very likely that our work suffers damage in its impaired quality. Moreover, this work has already gone through the sieve of two reviewers and an editor, and now we will have to reformulate the most sensitive parts of the work, already reformulated following their recommendations? On the other hand, we have seen in PeerJ many publications where the two topics are also presented together (see for example https://peerj.com/articles/matsci-2/, also published in the section 'Materials Science', in november 15, 2019, https://peerj.com/articles/achem-7/, published in the section 'Analytical Chemistry' in july 06, 2020, and https://peerj.com/articles/4464/ - of which I am co-author, published in march 6, 2018). There are also other studies where the authors chose to present the results and the discussion in a section that they called "Results". And that did not compromise the quality of these works. In view of the above, we ask you to reconsider the requirement made.

Sincerely,

Antonio Eduardo da Hora Machado, Prof. Dr.

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Laboratório de Fotoquímica e Ciência de Materiais

Responses to comments and/or suggestions:

Editor

Responses to comments done in the body of the text:

1) Would "bleaching" be a better term in this manuscript? (Abstract Line 14)

We prefer to keep the term "discoloration" because it is more widespread in this field of knowledge, which encompasses both studies concerning the photocatalytic detoxification of aqueous effluents and those that refer to the production of H_2 also via photocatalysis.

2) This is a parenthetical statement and should be punctuated accordingly (Line 51)

We agree. The sentence was changed as suggested.

3) Well-defined diffraction peaks is a direct observation, not an inference. The high crystallinity is an inference, however. (Line 185)

We agree. The term “high” was removed.

Reviwer#1

Answers to specific topics:

1) The sentence is confused. I suggest that the authors rewrite the sentence. *“The dyes discoloration was monitored without pH correction, by varying the absorbance of the solutions with the reaction time”.* (Line 139-140).

Our apologies. We agree that this sentence was confused. We changed it as suggested.

2) The reactor's boron silicate glass blocks a part of UV radiation. How intense is the radiation inside the reactor? (line 173).

The irradiance inside the reactor is 100 W/m^2, measured using a Detta OHM model HD 2102.2 radiometer equipped with a UV-A detector. The sentence was changed to: "Under this condition, its estimated photonic flux in the UVA was of 3.3 x 10^{-6} Einstein/s (Machado et al., 2008), with an irradiance inside the reactor of 100 W/m^2". (Lines 136-138).

3) I suggest adding Figure 1 to the supplemental material

We prefer to keep it as suggested in the original version of the work, because this figure portrays a photocatalytic system developed especially for the essays presented, thus deserving to be highlighted in the manuscript body.

4) I suggest removing the following sentence, as it does not contain any additional information. *"The average size of crystallites could not be calculated using the Debye-Scherrer method, since the presence of a second phase in the crystalline network creates considerable uncertainty in estimating this property (Kibombo et al., 2011)"*. (line195-197).

We agree. Thank you very much for the observation. This sentence and the related reference (lines 195-197 e 559-561, respectively, in the previous version of the manuscript) were removed.

5) Rewrite the following paragraph according to the discussion of the photocatalysis tests (323-332). "This may favor the adsorption of organic matter on their surfaces, which can consequently favor the photocatalytic efficiency. In addition, it was observed an inverse correlation between the surface area and the average particle size, except for the W1-25 that presented wide variation on its particle size*"*. (line 274-277).

This sentence was rewritten (lines 323 – 327 in the new version). Thank you for the contributions that have certainly given greater clarity to the presentation of our work.

6) TEM images show clusters of partially sintered nanoparticles with irregular shapes. What parameters were used in counting the particle size?

We considered that all nanoparticles were spheres-like, and we used the software "*ImageJ*", indicated in line 125 in the previous version of the article. This software allows through the zoom tool to measure small particles at the end of the cluster without loss resolution, as exemplified in the following figure,

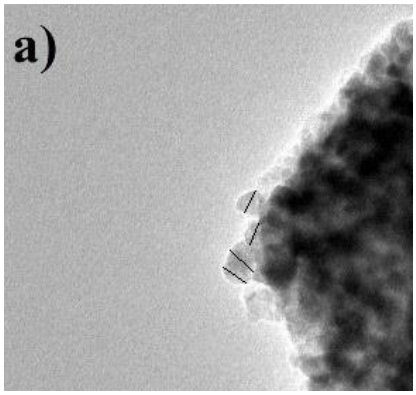

Figure - Example of measurements of measurements taken at the end of the image.

7) Has the adsorption capacity of the materials been analyzed?

In the present study, no adsorption measurements of the synthesized materials were done because we considered it irrelevant for the analysis of the results.

8) Was any characterization of the material carried out after the incorporation of the Pt?

An in-depth study on the photodeposition of Pt on the surface of TiO_2 was not developed, since this theme has been widely explored in other studies already published by other authors related to the production of H_2 via water splitting. The focus of this study was to demonstrate that the sol-gel synthesis combined with the use of acetone as co-solvent in the hydrolysis of the precursor (titanium tetraisopropoxide) causes a significant change in the proportion of crystalline phases (anatase/broquite), thus influencing the photocatalytic action of synthesized materials with regard to the ability to mediate the photocatalytic production of H_2. Pt was employed as a co-catalyst. We used a fixed

concentration so as not to mask the results of H_2 production of the different synthesized catalysts.

Reviwer#2

Answers to specific topics:

1) On page 5, line 123.

The sentence was corrected. Excuse us for this lack of attention, and thank you very much for the contribution.

2) On page 5, lines 141 and 142.

The experiments using the dyes P4R and RR120 were carried out separately and not using mixtures of these dyes. Thus, the monitoring of absorbance was performed separately. Therefore, there was no need to use calibration curves in spectrophotometric analyses of the discoloration of these dyes by photocatalytic route. We added in line 141 a sentence to clarify this.

3) On page 5, lines 150 to 152

In fact, losses occurred during washing and drying of the material after each photocatalytic cycle. However, there was no need to reduce the initial concentration of dyes proportionally to the recovered TiO_2 mass, because we used in all reuse tests the same mass used in the first assay. For this, four batch tests were performed for each cycle, in order to obtain an accumulated mass of recovered TiO_2 that guaranteed the same catalyst mass in the following cycles. We added to these lines a sentence to clarify this.

4) Figure 1

We agree. However, we believe that the reviewer here refers to Figure 2. We changed the colors to make the results presented adequately distinguishable. The internal captions have also changed in the new version of the figure.

Rietveld refinement for TiO_2-P25 was not performed since the constitution of this catalyst has already been widely studied in the literature. The focus of this work was the characterization of the new synthesized photocatalysts, which consists of anatase and broquite.

5) About Table 2

The error pointed out is persistent and occurred during the conversion of some files at the time of submission. On the substitution of the term "morphological parameters" by "textural parameters", we do not agree because the first is the most appropriate when studies involve solid materials.

6) About Table 3

> For each entry wherever the rate constants of discoloration or mineralization where presented, there are two values. It is not clear what these two values mean. Is it the result of two equal trials? If yes, I think it is more appropriate to present the data as an average and standard deviation. Or are those two values related to the two-stages pseudo-first-order rate constant? If yes, I recommend the authors to present these values in different columns, and clearly label the columns as first-stage degradation and second-stage degradation, for instance.

We did changes to the text between lines 323-331 to make it clearer. The kinetics presented for the discoloration and mineralization of the dyes used in this work as models of oxidizable substrates are all pseudo first order constants, representing processes that occur in two stages, except in the direct photolysis. Regarding the data, all constants presented are mean values related to at least three equivalent experiments, as stated in the experimental section (lines 133-153). Table 3 was redone including the R^2 of each regression analysis, as suggested.

> Second, for the RR120 dye, why is there only one value for the discoloration rate constant? The reason why there is only one value should be clearly explained by the authors.

The RR120 dye was completely discolored in just 80 minutes of reaction. Most likely, different from what occurs for P4R, the fragments, formed by the action of the radical species produced during the photocatalytic process, do not absorb or absorb radiation with very low efficiency at the wavelength in which the monitoring was performed (512 nm).

It should be emphasized that mineralization measures were conducted monitoring the dissolved organic carbon, much more accurate than discoloration measurements.

> Third, why were the samples W1-25 and W1-75 not tested neither for mineralization nor discoloration for RR120? If the authors have the possibility to perform this analysis, they should timely do it for the revisions of this paper. If the authors are unable to do it, the reason why should be clearly explained in the manuscript text.

Although the mineralization and discoloration of P4R conducted using W1-75 presented the best performance among the synthesized oxides, this result was only 4.8% higher than that achieved when using the W1-50, to the detriment of the expressive amount of acetone used in the synthesis of W1-75. In view of this, W1-50 was considered as the most effective catalyst for mineralizing P4R, being therefore preferably applied in the following stages of the present study. W1-25 and W1-75 did not have their discoloration and mineralization efficiencies evaluated by the reason exposed between lines 337-346, in the body of the article, whose sentences were duly improved. As W1-50 was defined as the catalyst with the best performance, only it was evaluated in the reuse and photocatalytic production tests of H_2.

> Fourth, to complement the data, I recommend the authors to present the R_2 values obtained from the pseudo-first-order model fit to the experimental data.

Table was improved.

> Fifth, the caption should be checked, as it is showing Table 1 instead of Table 3.

As pointed out above, this error is persistent and occurred during the conversion of some files at the time of submission.

7) About the mineralization and discolaration kinetics:

We appreciate the suggestion, but we do not see the need to use non-linear fitting to the data to confirm that both discoloration (excluding data for RR120 using W1, W-50 and P25) as mineralization usually occurs in two stages in pseudo-first order kinetics, as suggested by the kinetic treatment we applied to the collected data. We emphasize that this form of data processing is the result of previous studies conducted by our research group. A more detailed discussion of this treatment can be found, for example in the reference (França et al., 2016; doi: 10.5935/0103-5053.20160007) cited in the present study.

We are sure that, through these tests, our goal of defining the most appropriate catalyst, among which we synthesize, for application in hydrogen production tests, was achieved.

However, we do not rule out the possibility of applying the suggested treatment in future studies.