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Referee's Report
of the Ph.D. Thesis of **Mr. Abdul Qayyum**

done at the Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

under the supervision of Prof. dr hab. eng. Juan Carlos Colmenares Quintero

The Ph.D. Thesis of Mr. Abdul Qayyum entitled:

"Titania-based photocatalysts prepared by sonication in understanding the selective oxidation of lignin-inspired molecules to phenolics", contains 141 pages (20 + 121) – including: cover page with the title, dedication to Allah, acknowledgement, funding, declaration of originality, list of scientific papers co-authored by Mr. A. Qayyum, information about invited chapter, list of participation in scientific conferences, list of abbreviation, list of units, abstract (in English and in Polish), table of contents, and main part of the Thesis: introduction, research hypothesis and goals, methodology, results and discussion, summary and future perspectives, references. Presented material is illustrated by figures, tables, schemes and equations. In a brief summary it can be presented as follows:

Table 1. Statistic of the evaluated Thesis.

	Number of				
Chapter	figures	tables	schemes	equations	references
1. Introduction	9	-	-	-	-
2. Research hypothesis and goals	-	-	-	-	-
3. Metodology	1	1	1	10	-
4. Results and discussion	37	8	2	-	-
5. Summary and future perspectives	-	-	-	-	-
Total	**47**	**9**	**3**	**10**	**186***

* reference [70] is the same as [118]

As a Referee I should give some comments, and they are mainly related to the presentation of the results obtained. In general, my opinion about the Ph.D. Thesis level is very high. Please find included below some selected examples.

Abstract presented at the beginning (pp xv-xviii, in English and in Polish, respectively) gives short summary of the Thesis content. However, at this point there is no clear indication what was the aim and objectives of the studies conducted. This was described in the chapter two, where the Author presented four research hypotheses, whose accuracy should be confirmed by carrying out research related to the presented key objectives. Aims and objectives of the Thesis ought to correlate with the final conclusions. That is why it is important to specify the goals of the undertaken research. It is good that goals and tasks were set before the experimental part.

All research hypotheses, taking into account the assumed key objectives, were systematically tested, and the results of these studies were presented in the chapter four. Each stage of the research was presented and discussed, taking into account the cited literature. It is worth emphasizing that after each of these stages a summary and conclusions were presented. Moreover, some of the results were published already or submitted for publishing in reputable journals with international circulation.

Experimental section (Chapter 3: Methodology) is an integral and very important part of the Thesis. Here ought to be given all details connected with the experiments methodology. This has been elaborated by the Author well. All necessary information related to: materials, syntheses and physicochemical characteristics have been provided. The synthesized photocatalysts were characterized by various techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), nitrogen sorption (for the porosity), and diffused reflectance spectroscopy (DRS) to estimate the optical band gap. The synthesized photocatalysts were tested for the additives-free photocatalytic selective conversion of lignin inspired model compounds such as the benzyl alcohol and 2-phenoxy-1-phenylethanol in the bath catalytic reactors.

All main conclusions of the PhD Thesis (Chapter 5, pp 95-97) are in full compliance with the research hypotheses presented earlier. I completely agree with the Author that "*all the results and the discussion presented that ultrasonication (US) can be used as a green-oriented approach for the synthesis of the nanomaterials by avoiding the energy-demanding approach, such as calcination steps*". In general, this is consistent with the broader idea of sustainable development. The main part of the Thesis is ended with the future perspectives.

The research was carried out on a laboratory scale, using, say, a model system. From a scientific point of view, the work is very interesting and valuable. However, I am interested in the prospects for the practical application of the results obtained:

- What is the possibility of increasing the scale to semi-technical and then to industrial?
- Is it economically profitable?
- Has the Author considered LCA (Life Cycle Assessment) for the selected model system?

I do not expect an exact answer, but only the doctoral student's opinion on the questions asked.

In my opinion any graphic presentation should be named as a figure. The Author of the Thesis used two, however logical, versions: schemes and figures.

Mr. A. Qayyum used many abbreviations in the text of the dissertation. They are presented at the beginning of the Thesis (pp xi-xii), and they are not given in an alphabetical order.

This makes it a bit difficult to use the attached list. The same problem is with list of units (pp xiii-xiv).

as in Ph.D			ought to be	
TiO_2	titanium dioxide		$AgNO_3$	silver nitrate
UV	Ultraviolet		BET	Brunauer Emmett Teller
US	ultrasound		BJH	Barret Joyner Halenda
Xe	Xenon		BQ	1,4-benzoquinone
N_2	nitrogen		CO_2	carbon dioxide
BET	Brunauer Emmett Teller		DSC	Differential Scanning Calorimetry
BJH	Barret Joyner Halenda		e^-	electron
UV-Vis DRS	Ultraviolet-Visible Diffuse Reflectance Spectroscopy		EDXRF	Energy Dispersive X-ray Fluorescence
			FID	Flame Ionization Detector
XRD	X-ray Diffraction		GC	gas chromatograph
TEM	Transmission Electron Microscopy		h^+	hole
HAADF-STEM	High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy		HAADF-STEM	High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis		He	helium
XPS	X-ray Photoelectron Spectroscopy		HF	heat flow
TPD	Temperature Programmed Desorption		KI	potassium iodide
TPO	Temperature Programmed Oxidation		LEDs	Light Emitting Diodes
He	helium		N_2	nitrogen
O_2	oxygen		O_2	oxygen
Ph-CH_2OH	benzyl alcohol		$O_2^{\bullet-}$	super oxide anionic radical
PP-ol	2-phenoxy-1-phenylethanol		OH	hydroxyl
LEDs	Light Emitting Diodes		●OOH	hydrogen superoxide radical
PP-one	2-phenoxy-1-phenylethanone		Ph-CHO	benzyl aldehyde
Ph-OCHO	phenyl formate		Ph-CH_2OH	benzyl alcohol
Ph-OH	phenol		Ph-OCHO	phenyl formate
Ti	titanium		Ph-OH	phenol
KI	potassium iodide		PP-ol	2-phenoxy-1-phenylethanol
h^+	hole		PP-one	2-phenoxy-1-phenylethanone
BQ	1,4-benzoquinone		Rh	rhodium
$O_2^{\bullet-}$	super oxide anionic radical		t-BtOH	tert-butanol
t-BtOH	tert-butanol		TEM	Transmission Electron Microscopy
OH	hydroxyl		TGA	Thermal Gravimetric Analysis
$AgNO_3$	silver nitrate		TPD	Temperature Programmed Desorption
e^-	electron		TPO	Temperature Programmed Oxidation
GC	gas chromatograph		Ti	titanium
Ph-CHO	benzyl aldehyde		TiO_2	titanium dioxide
DSC	Differential Scanning Calorimetry		US	ultrasound
HF	heat flow		UV	Ultraviolet
CO_2	carbon dioxide		UV-Vis DRS	Ultraviolet-Visible Diffuse Reflectance Spectroscopy
EDXRF	Energy Dispersive X-ray Fluorescence			
●OOH	hydrogen superoxide radical		Xe	Xenon
Rh	rhodium		XPS	X-ray Photoelectron Spectroscopy
FID	Flame Ionization Detector		XRD	X-ray Diffraction

Remarks and comments presented above are not those, which may disqualify the entire Thesis. It is just job of the referee.

I would like to underline that the Author has quoted 186 literature references and many of them are cited in the experimental part of the Thesis (including results and discussion). Moreover, most of them are from the last two decades (above 84%), which means they are very up to date. Below I present graphical statistic of the references quoted in the Thesis.

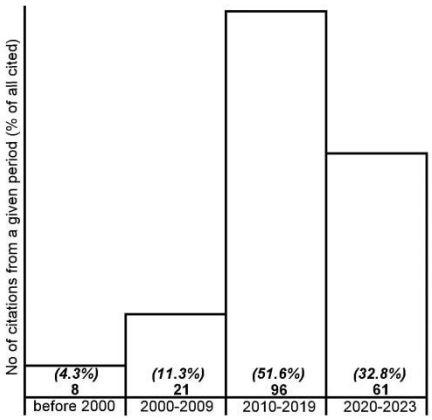

Fig. 1. Graphical statistic of the references quoted in the Mr. Abdul Qayyum Thesis.

An introduction contains condense review of the literature connected strongly with the experimental part.

Experimental data presented in form of tables and figures indicate clearly that enormous work has been done. It took a lot of work and many hours spent in the lab.

Mr. A. Qayyum is a co-author of six scientific papers:

1. D.A. Giannakoudakis, **A. Qayyum**, D. Łomot, M.O. Besenhard, D. Lisovytskiy, T.J. Bandosz, J.C. Colmenares, Boosting the photoactivity of grafted titania: ultrasound-driven synthesis of a multi-phase heterogeneous nano-architected photocatalyst, *Advanced Functional Materials*, **31**/1 (2021) 2007115; DOI: 10.1002/adfm.202007115 (**IF=19.924**)
2. D.A. Giannakoudakis, **A. Qayyum**, V. Nair, A. Khan, S.R. Pradhan, J. Prekodravac, K. Rekos, A.P. LaGrow, O. Bondarchuk, D. Łomot, K. Triantafyllidis, J.C. Colmenares, Ultrasound-assisted decoration of CuO_x nanoclusters on TiO_2 nanoparticles for additives free photocatalytic hydrogen production and biomass valorization by selective oxidation, *Molecular Catalysis*, **514** (2021) 111664; DOI: 10.1016/j.mcat.2021.111664 (**IF=5.089**)
3. **A. Qayyum**, D.A. Giannakoudakis, A.P. LaGrow, O. Bondarchuk, D. Łomot, J.C. Colmenares, High-frequency sonication for the synthesis of nanocluster-decorated titania nanorods: making a better photocatalyst for the selective oxidation of monoaromatic alcohol, *Catalysis Communications*, **163** (2022) 106406; DOI: 10.1016/j.catcom.2022.106406 (**IF=3.7**)
4. D.A. Giannakoudakis, F.F. Zormpa, A.G. Margellou, **A. Qayyum**, R.F. Colmenares-Quintero, C. Len, J.C. Colmenares, K.S. Triantafyllidis, Carbon-based nanocatalysts (CnCs) for Bbiomass valorization and hazardous organics remediation, *Nanomaterials*, **12**/10 (2022) 1679; DOI: 10.3390/nano12101679 (**IF=5.3**)
5. D.A. Giannakoudakis, **A. Qayyum**, M. Barczak, R.F. Colmenares-Quintero, P. Borowski, K. Triantafyllidis, J.C. Colmenares, Mechanistic and kinetic studies of benzyl alcohol photocatalytic oxidation by nanostructured titanium (hydro) oxides: do we know the entire story? *Applied Catalysis B: Environmental*, **320** (2023) 121939; DOI: 10.1016/j.apcatb.2022.121939 (**IF=24.319**)
6. **A. Qayyum**, D.A. Giannakoudakis, D. Łomot, R.F. Colmenares-Quintero, A.P. LaGrow, K. Nikiforow, D. Lisovytskiy, J.C. Colmenares, Tuning the physicochemical features of titanium oxide nanomaterials by altering the ultrasound parameters during the synthesis: elevating photocatalytic selective partial oxidation of aromatic alcohols, *Ultrasonics Sonochemistry*, **94** (2023) 106306; DOI: 10.1016/j.ultsonch.2023.106306 (**IF=9.336**)

and one is submitted for publishing:

7. **A. Qayyum**, D.A. Giannakoudakis, D. Łomot, R.F. Colmenares-Quintero, A.P. LaGrow, K. Nikiforow, J.C. Colmenares, Selective (sono)photocatalytic cleavage of lignin-inspired β–O–4 linkages to phenolics by ultrasound derived 1-D titania nanomaterials, *ACS Sustainable Chemistry and Engineering* – submitted (IF=9.224)

Above mentioned scientific articles were published in the international journals with a high impact factor (IF in the range 3.7 to 24.319; an average IF per published paper is about 11.278).

Moreover, He has an active participation in scientific conferences:

1. **A. Qayyum** *et al.*, *Ultrasonic-assisted synthesis of nanostructured TiO_2: photocatalytic selective oxidation of benzyl alcohol to benzyl aldehyde*, **5th EuChemS Conference on Green and Sustainable Chemistry (5th EuGSC)** with an organized by the Association of Greek Chemists (AGC) and EuChemS /Division of Green and Sustainable Chemistry which held virtually on 26th – 29th September 2021, **oral presentation.**
2. **A. Qayyum** *et al.*, *Titania-based photocatalytic selective cleavage of C–C bond of a lignin-based model compounds*, **54th National Catalytic Colloquium**, held at the Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Cracow, Poland on 1st – 3rd June 2022, **oral presentation.**

3. **A. Qayyum** *et al.*, *Key role of ultrasound on the synthesis of TiO_2 nanomaterials and catalytic performance*, **The 9th IUPAC International Conference on Green Chemistry (9th ICGC)**, held at Zappeion Megaron, Athens, Greece on 5th – 9th September 2022, **oral presentation.**
4. **A. Qayyum** *et al.*, *Optimization of the ultrasonic power during synthesis of TiO_2 to elevate the photo(sono)catalytic activity for additive-free partial selective oxidation of benzyl alcohol to benzyl aldehyde*, **6th Green & Sustainable Chemistry Conference**, organized by Elsevier which held virtually on 16th – 18th November 2021, **poster presentation.**
5. **A. Qayyum** *et al.*, *Photocatalytic selective oxidation of lignin-based molecule benzyl alcohol to benzyl aldehyde by different Nano-morphologies of TiO_2*, **11th European Conference on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA)**, held in Turin, Italy, on 6th – 10th June 2022, **poster presentation.**
6. **A. Qayyum** *et al.*, *Photocatalytic selective oxidative cleavage of β-O-4 linkages of a lignin-based model compounds by novel TiO_2 nanomaterials*, **15th European Congress on Catalysis**, held at Prague Congress Centre, Prague, Czech Republic, on 27th August – 1st September, 2023, **poster presentation.**

Nowadays scientific work is a complex one and have to be done in a group. In an acknowledgements part Mr. A. Qayyum show that He fully understand this. This confirms His scientific maturity. The success of one person is a success of the whole cooperating team. I greatly appreciate main acknowledgement and dedications addressed to Allah and family, respectively. From the scientific point of view it is not a part of the Thesis but just strong and valuable connection between science, personal life and religion. Very important and worth emphasizing.

According to the contents and form of presentation of the **Mr. A. Qayyum** Thesis, I would like to inform that in my feeling He could be a promising person for the research continuation.

I hope that the full set of the results (not published yet) elaborated according to the standard of an appropriate scientific journal will be published soon, to be available in a broad sense for the scientific community.

In my opinion, the Thesis of Mr. A. Qayyum fulfils all the requirements for the Ph.D. degree in chemistry. I wish Him personal and scientific success in the following steps of the procedure.

J. Ryczkowski

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