



Confidential

Review of USB FFPW PhD Thesis

First name(s), surname, titles of the PhD student: Syam Krishna B., M.Sc.	First name(s), surname, titles of supervisor: Prof. RNDr. Petr Špatenka, CSc.
Title of PhD thesis: Degradation of organic pollutants in water by non thermal plasma based advanced oxidation processes	
REVIEWER:	
Surname: Klusoň	Institution: Institute of Chemical Process Fundamentals, AS CR
Name: Petr	
Titles: Assoc. Prof. Dipl.-Ing., Ph.D.	E-mail: Kluson@icpf.cas.cz
Please describe your professional relationship to the PhD student: There have been no relationships in the past.	Please describe your field of expertise: Processes for environment, environmental chemistry, catalysis, reaction engineering.

QUESTIONNAIRE

Originality, scientific importance, perspectives and impacts of results presented in the PhD thesis for basic and/or applied research

Evaluate competitiveness of the PhD thesis in the international context and compare its level with the current state of the art in the field (**extent ¼ – ½ page**):

The work is fully competitive, it addresses a very modern topic, the expected impacts are high. More details could be found in the full text review below.

Elaboration of the PhD thesis, objectives of the work and deliverables

Evaluate the overall level of elaboration of the PhD thesis (structuring of the main text, comprehensibility, logicity of the chapters and their ordering) and the originality of the selected approaches to solve the objectives; evaluate publications and whether the results described correspond to objectives of the PhD thesis (**extent ¼ – ½ page**):

The work meets all standards required for the good and matured scientific work. More details could be found in the full text review below.

OVERALL COMMENTARY ON THE PhD THESIS

Please write comments in extent of 1-2 pages:

Referee Report

The Dissertation Thesis entitled *Degradation of organic pollutants in water by non-thermal plasma based advanced oxidation processes* by Mr. Syam B. Krishna, M.Sc, B.Sc represents, no doubts, a good and matured scientific work. It is divided into six chapters. Each of them focuses on a specific topic. The Thesis is logically organized, well structured, and bringing enough details on the discussed phenomena. The work is written only with minor extent of formal errors, the used English is also on a good level, the cited literature is relevant and well descriptive. In the first chapter general information on the methods for reducing water pollution is treated in a comprehensive way. The chapter complies well with all requirements for the Theoretical Part. Details on standard methods are briefly mentioned, and logically confronted with advanced oxidation processes. In the next part of this chapter plasma assisted methods are carefully introduced, pointing mainly on their advantages in comparison with standard approaches relying also on evolution of highly reactive radicals. In this respect special attention is paid to the gliding discharge, corona discharge, and barrier discharge.

In the next chapter (II) the author deals with the model water treatment polluted with atrazine and hydrocortisone via the application of non-thermal plasma, the dielectric barrier discharge. The text has an appearance of a finished manuscript of a paper, and it seems that it is ready for submission. The construction of the DBD reactor is properly introduced, along with optimized process conditions. Special attention is paid to the mechanisms of both model compounds degradations, and to the kinetics of their decomposition. Drawn conclusions are clear, and well justified.

The chapter III is presented in a form of paper which was already published in Chem. Eng. J. As this journal is known for its strict and tough peer review procedure, involving at least two referees, the text is supposed to be already formally as well as scientifically well shaped. The paper deals with "Products and mechanism of verapamil removal in water by air non-thermal plasma treatment".

It is the same story for the chapter IV and the text entitled "Degradation of verapamil hydrochloride in water by water gliding arc discharge". In this case the paper was published in prestigious Chemosphere.

In chapter V the results, and discussion are also already shaped to the paper form. The treated topic is entitled "Degradation of organic pollutants in water by advanced oxidation processes". The paper brings, among others, a special focus on ozonation, which was identified as an extremely effective method towards the decomposition of certain specific water pollutants.

The final chapter (VI) could be referred to as a kind of summary and concluding remarks and notes. It is well written, it's content is fully appropriate.

The next points should be addressed during the Thesis discussion upon the defence.

1. Could you kindly specify in more details the selection strategy for choosing the particular model pollutants – atrazine, hydrocortisone, and Verapamil.
2. Is it possible to assess critically the cost for processing 1 l of polluted water and treated with the studied methods?
3. Could you operate your systems in fully continuous manner?
4. What effectivity of the methods would you expect for main stream synthetic steroids?
5. The kinetic models are defined only in a vague way. What reactions orders were assumed?
6. Is it possible, from principle physical reasons, to cross-compare the rate constants between processes with different plasma sources?
7. Did you pay more attention to assess the life time of evolved radicals?
8. What was the reason for relatively very high stability of hydrocortisone? Is it a common feature of such molecular structures?
9. Could you, in a physical and/or chemical sense, explain why ozonation reveals such an extraordinary efficacy towards the described reactions?
10. Are there mechanism differences?

The Dissertation Thesis of Mr. Syam B. Krishna, M.Sc, B.Sc meets all standards and requirements for the Ph.D. work at Czech Universities. I fully support the recommendation for the final defence.

FINAL RECOMMENDATION

- PhD Thesis can be recommended for defence
 PhD Thesis can be recommended with reservations for defence
 PhD Thesis can not be recommended for defence

14.6.2017

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Date and place

Praha



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Name and signature



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Review of USB FFPW PhD Thesis

First name(s), surname, titles of the PhD student: Syam Krishna B., M.Sc.	First name(s), surname, titles of supervisor: Prof. RNDr. Petr Špatenka, CSc.
Title of PhD thesis: Degradation of organic pollutants in water by non thermal plasma based advanced oxidation processes	

REVIEWER:

Surname: Dors	Institution: Institute of Fluid Flow Machinery, Polish Academy of Sciences Fiszera 14, 80-231 Gdańsk, Poland
Name: Miroslaw Wojciech	E-mail: miroslaw.dors@imp.gda.pl
Titles: Ph.D., D.Sc.	
Please describe your professional relationship to the PhD student: No relationship	Please describe your field of expertise: plasma physics and chemistry, non-thermal plasma applications for environment protection

QUESTIONNAIRE

Originality, scientific importance, perspectives and impacts of results presented in the PhD thesis for basic and/or applied research

Evaluate competitiveness of the PhD thesis in the international context and compare its level with the current state of the art in the field (**extent ¼ – ½ page**):

The thesis contains valuable original results on the chemistry and technology of plasma treatment of waste water contaminated with complex chemical compounds. The research field is relatively new and there is a need to study kinetics and mechanisms of degradation of many different chemicals present in waste and surface water. Results obtained by the Ph.D. candidate give new information as well as they confirm general hypothesis on the main role of hydroxyl radicals in the degradation process of organic pollutants.

Importance of results presented in the thesis concerns not only basic but also applied research because they show efficiency of pollutants degradation in several plasma-based methods. For that reason they are useful for researchers designing and studying plasma reactors and plasma technologies for water treatment.

Two papers included in the thesis were published in 2016 and so far they have been cited once (each) by other scientists but it seems that due to their scientific value the number of citation will grow in time.



Elaboration of the PhD thesis, objectives of the work and deliverables

Evaluate the overall level of elaboration of the PhD thesis (structuring of the main text, comprehensibility, logicity of the chapters and their ordering) and the originality of the selected approaches to solve the objectives; evaluate publications and whether the results described correspond to objectives of the PhD thesis (**extent ¼ – ½ page**):

The thesis is well organized and comprehensive. The structure and content of General Introduction is adequate to the topic and following chapters. Objectives are well chosen and structured logically, however they could be written more like goals than a road map (for example, "Determination/description of degradation kinetics ..." instead of "Investigation of degradation kinetics ..").

The Author carried out some experiments in collaboration with research teams from Italy and Poland which have been active in the field of plasma applications for many decades. That is why research methods used for achieving objectives stated in the thesis were appropriate. Using HPLC/MS for water diagnostics is common and best available technique. The same in the case of using optical emission spectroscopy (OES) for plasma diagnostics. The thesis gives a complete picture on the chemistry of selected pollutants in spite of the fact that all described analytical methods were not used in all experiments. In the case of DBD and ESD no OES was applied. On the other hand, samples taken after GAD, ESD and ozonation were not analyzed for TOC. However, it is not a weakness of the thesis and the information obtained in experiments is enough for describing degradation mechanisms of pollutants used the work. This case was also not raised by reviewers of publications given as Chapter 2 and 3. As for publications, it would be worthwhile to publish Chapter 2 and 5 as separate papers in international journals because of the high value of the results presented in those chapters.

It is worth emphasizing a strength of the thesis which is Chapter 6 General Discussion. Together with conclusions it hits the nail on the head of the problem concerning using plasma for water treatment and shows a level of mature researcher. There are also no doubts that results presented in the thesis correspond to objectives.

OVERALL COMMENTARY ON THE PhD THESIS

Please write comments in extent of 1-2 pages:

The thesis fulfils the internal rules of the Faculty (Act. No. 09/0705/16). It is written thoroughly and only a few editorial errors can be found:

- Page 13: In the sentence "It has been suggested that electrical discharges with longer pulse duration ..." it should be "shorter pulse",
- The last sentence in page 72 is completely unclear. It looks like two sentences mixed.

State-of-the-art, at least for the plasma part, is presented well and references are adequate. Other essential parts of the thesis, i.e. motivation, objectives, results and conclusions are also clearly and adequately presented. It is worthy emphasizing that Ph.D. candidate determined several factors concerning plasma methods/technologies for water purification: degradation kinetics, degradation mechanism, degradation efficiency and its energy yields. First two factors are important for scientists interested in fundamental chemistry whereas the other two factors are crucial for

technologists.

Detailed comments:

1. All types of electrical discharge used for the thesis produce non-thermal plasma. Thus, the title of each chapter should be more specific, e.g. Chapter 2 DEGRADATION OF ATRAZINE AND HYDROCORTISONE IN WATER BY DIELECTRIC BARRIER DISCHARGE TREATMENT, Chapter 3 PRODUCTS AND MECHANISM OF VERAPAMIL REMOVAL IN WATER BY DIELECTRIC BARRIER DISCHARGE TREATMENT, Chapter 5 DEGRADATION OF ORGANIC POLLUTANTS IN WATER BY ELECTROHYDRAULIC SPARK DISCHARGE).
2. Why degradation by-products of atrazine during spark discharge could not be detected? Were they not present or not appropriate HPLC/MS configuration was used?
3. What about nitrated and nitrosated by-products in GAD? Since air was used as the working gas one may expect formation of such products.
4. Curve fitting in figures showing changes in concentrations of degraded pollutants can be questionable. There are too few data points to do it properly. It would be better to connect them with straight lines or not using lines and fitting at all. The problem is well seen especially in Fig. 1 of the publication in Chapter 3. Fitted curve concerning initial concentration of 1×10^{-5} M suggests complete degradation of Verapamil after ca. 60 minutes whereas, as seen from data points, it may be after 30 min. The same for higher concentration: fitted curve suggests 140 min but the last data point suggests 100-110 min.
5. All curve fittings were done assuming pseudo-first order kinetics. The order would be better seen in figures prepared in logarithmic scale (Y axis as $\ln[c_0/c]$). Then, it could reveal that the order is 1.5 or 2 rather than 1. That would imply further discussion about degradation mechanisms.
6. Page 72 – "...in the process induced by the electrode configuration adopted for our reactor." In a plasma reactor processes are induced by electrical discharge not by electrode configuration. Thus, the sentence should end with "... in the process induced by electrical discharge generated in our reactor".
7. Mineralization by ozone is a subject for wider discussion. A part of researchers claim that it is possible (as was shown in Chapter 3) but the others are sure that ozone cannot oxidize complex organic pollutants into CO_2 and H_2O . This was not stated clearly in the thesis but it seems that Ph.D. candidate is aware of the problem. In page 74 he suggests "ozonation as a pre-treatment method to enhance biodegradability and reduce toxicity of the industrial effluents, followed by biological treatments".

Generally, the thesis shows that its Author gained the level of mature researchers. Results of experiments he carried out are valuable and important for scientists dealing with plasma chemistry and plasma applications. Future investigations proposed at the end of the thesis are interesting and worth taking and they are logical continuation of experiments described in the thesis.



Fakulta rybnářství
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Faculty of Fisheries
and Protection
of Waters

Jihočeská univerzita
v Českých Budějovicích
University of South Bohemia
in České Budějovice
Czech Republic

FINAL RECOMMENDATION

- PhD Thesis can be recommended for defence**
- PhD Thesis can be recommended with reservations for defence**
- PhD Thesis can not be recommended for defence**

2017/06/13 Gdovish, Plesud
.....
Date and place

Miroslav Dvořák
.....
Name and signature
