

Confidential

Review of USB FFPW PhD Thesis

First name(s), surname, titles of the PhD student: Oksana Golovko, M.Sc.	First name(s), surname, titles of supervisor: M.Sc. Roman Grabic, Ph.D.
Title of PhD thesis: Pharmaceuticals and other human used chemicals in water environment – stability and fate	
REVIEWER:	
Surname: Bodík	Institution: Slovenská technická univerzita v Bratislavě Radlinského 9 812 37 Bratislava Slovak Republic
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Titles: Assoc. Prof. Dipl.-Ing., CSc.	
Please describe your professional relationship to the PhD student: ---	Please describe your field of expertise: Biological wastewater treatment processes, biogas production from biowaste,

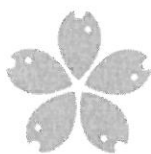
QUESTIONNAIRE

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 presented PhD. thesis of M.Sc. Oksana Golovko deals with the very actual topic of pharmaceuticals and human used chemicals monitoring in water environment. The subject of the thesis is up to date, it corresponds with the modern trends in water/wastewater chemistry field in the recent years. The results of the present work represent really new information in the monitoring and behaviour of PPCPs in the environment of wastewater treatment plants and surface water bodies. The results from the paper "Storage effect on the analysis of PPCPs in wastewater" represent a very important tool for analytical laboratories, how to organise sampling and storage of wastewater samples. The data from characterisation of seasonal effect on concentration and removal efficiency of PPCPs in WWTPs have also very high originality and scientific importance level. This information about the removal and seasonal variability of some pharmaceuticals (norfloxacin, ciproxacin, oxazepam, UV-filters etc.) are, probably, the first scientific report focused on this group of compounds.

High scientific level of the PhD-thesis is confirmed also by the acceptance and publishing of laboratory results in prestigious international journals (Chemosphere, Environmental Science and Pollution Research as well as in Surface and Coatings Technology). Publishing in such



journals ensures the originality and scientific importance of published works and also gives high suppositions for citation of these works in scientific journals.

Besides the theoretical basic research importance of measured results (monitoring and seasonal variation of PPCPs in water environment) the PhD-thesis offers on the other hand, a “practical application” and technology results useful for removal of such type of compounds in natural water (AOPs to removal of resistant chemical compounds). I highly appreciate this part of the thesis because it makes the optimal balance of presented results between basic and applied research.

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**):

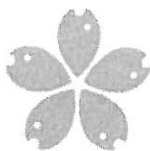
The presented PhD. thesis of M.Sc. Oksana Golovko is focused on the actual and, in present time, very discussed topic of the presence and removal of emerging chemical compounds in water environment. The text of the thesis has 95 pages including many tables, graphs and additional information (List of publications, CV etc.). The thesis consists of five main chapters. The first chapter is a general introduction with a short literature review relevant to the thesis topics. Relatively short (in my opinion) but an important part of the introduction is the subchapter Aims of the present study, where the main objectives of this study have been described. The choice of the aims was realised according to main thesis topics and is acceptable.

The Chapters 2-4 consist of five inserted papers published (four of them) in scientific international journals. The papers are divided into chapters according to topics of papers.

The last Chapter 5 includes individual texts summarising the experimental results presented in published papers (English and Czech Summary) as well as texts with some personal data of the PhD student (list of publications, CV etc.)

The presented PhD thesis has a logical structure and the form and editing of the thesis are of a very high quality. I am not capable to evaluate accurately the language level; nevertheless, the text is clear and easily understandable.

The presented experimental results and the list of publications confirm also a very high scientific level of the Faculty of Fisheries and Protection of Waters as well as a fruitful international contacts and cooperation in the field of environmental chemistry and monitoring. All the aims defined at the beginning of the study were achieved. The author has shown deep knowledge of the investigated areas and ability to pursue independent and efficient research work.



OVERALL COMMENTARY ON THE PhD THESIS

Please write comments in extent of 1-2 pages:

Chapter 1

Comprehensive literature research on PPCPs focused on basic information about determination of PPCPs in an aquatic environment by liquid chromatography coupled to mass spectrometry as well as on occurrence and fate of PPCPs in wastewater and surface water.

Comment:

- many times is WWTP declared in PhD thesis as an "important source of PPCPs in water". I think it is not "fair" to WWTP, because the original pollution source is somewhere before the inlet of wastewater into WWTP.

Chapter 2-4

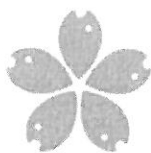
All papers added in the PhD-study were issued in international scientific journals, where undergone through peer-reviewed processes. This process guarantees the quality of paper manuscript, as well as the right interpretation of measured data a conclusions. In the followed text I would like to summarise and to comment of published papers with evtl. short questions and remarks.

Chapter 2

The stability and the impact of long-term storage of 124 target analytes in influent and effluent wastewater is described in this chapter (one scientific paper in Chemosphere). Short-term (7 days) stability was checked by comparing samples at 4 °C and -18 °C and also the long-term (60 and 120 days) stability was compared by samples stored at -18 °C. The results of this part of PhD thesis showed that multi-residue analysis of wastewater samples is always a compromise concerning not only the analytical method and extraction procedure, but also the choice of storage conditions. Very interesting result is that for the short-term storage, keeping the samples in fridge (4 °C) showed better results than freezing/thawing procedure. Based on these findings, it would be better to analyse samples as soon as possible. This result could be very useful for many laboratories dealing with PPCPs analyse in wastewater.

Questions:

- The concentration of suspended solids in the influent of the WWTP is within the concentration range of 200 – 350 mg/l, but in the effluent is within the range of 10 – 15 mg/l (almost filtered sample). How could the process of freezing/thawing influence on such different samples?
- Is the pre-treatment process of samples with high SS concentrations more important than with low SS concentration samples?
- Is there some literature information about the influence of desorption (increasing of concentration in solution) during freezing/thawing procedure on the final concentration of PPCPs compounds?



Chapter 3

Many of PPCPs are frequently detected in WWTPs, however, little is known about the concentration changes of these compounds in wastewater during the year. Just on this gap in international scientific literature, two papers from Chapter 3 were focused. Seasonal removal efficiency and variation of 16 + 21 types of PPCPs were monitored in a WWTP České Budějovice. Paper „Seasonal changes in antibiotics, antidepressant/psychiatric drugs, antihistamines and lipid regulators in WWTPs examined the long term variations of selected PPCPs in WWTP in České Budejovice. This work is probably the first scientific paper reporting the seasonal variations of many PPCPs in municipal WWTPs (norfloxacin, ciprofloxacin, levofloxacin, etc.) during whole year. The paper from journal ESPR supplements the list of monitored pharmaceutical compounds with analgesics, anti-hypertensive and UV-filters. Provided data on PPCPs variations and removal efficiency would add relevant literature information for further assessment of wastewater and natural water pollution.

Remarks:

- You identified some compounds with negative removal efficiency (Chapter 3) and on the other hand, compounds with positive increase of concentration during the storage experiments (Chapter 2). Could you identify some relations between both groups? Are there the same compounds?
- the calculation formula for removal efficiency is wrong (chapter 3.2.)

Chapter 4

To overcome the problem of insufficient elimination of PPCPs during treatment, advanced oxidation processes (AOPs) were tested in the last chapter of PhD study. The photo degradation of pharmaceuticals has been studied in buffer water under UV and sunlight. The rate of photolysis was slower under UV exposure for most of pharmaceuticals. It was confirmed that photo transformation reactions could play an important role in the elimination of some pharmaceuticals from surface waters.

Remarks

- How do you see the real application of photo degradation processes in surface water, how could it be intensified.
- Why are not the photo degradation processes well applicable on a real WWTP?

Chapter 5

In the Chapter 5 the results from whole PhD thesis are shortly discussed and confronted with relevant literature. The discussion has a logical line and real conclusions.




Fakulta rybnářství
a ochrany vod
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**

10th June, 2014
Date and place


...Ass.Prof. Igor Bodík, PhD.
Name and signature



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Review of USB FFPW PhD Thesis

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Title of PhD thesis: Pharmaceuticals and other human used chemicals in water environment – stability and fate	
REVIEWER:	
Surname: Grochowalski	Institution: Cracow University of Technology Politechnika Krakowska Warszawska 24 St. 31-155 Kraków, Poland
Name: Adam	E-mail: agrochow@chemia.pk.edu.pl
Titles: Dr. hab. Ing,	
Please describe your professional relationship to the PhD student: no relationship	Please describe your field of expertise: analytical chemistry, environmental chemistry, waste disposal and waste treatment technologies

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 presented PhD thesis put a new light on the very actual problems concerning the fate of modern pharmaceuticals and personal care products and contemporary possibilities of decomposition of these compounds in wastewater treatment plants. It should be emphasized, that, however, there are many scientific work performed and published in such area - the presented work is novel and gives a big number of data for both: analytical activities (durability test samples) as well as seasonal variations and the stability of PPCPs in the aquatic environment.

It gives quite new information about fate of this particular contaminant in aquatic ecosystem.

The experiments have provided a lot of extremely valuable data which may be useful for the routinely control of polar environmental pollutants using up-to-date analytical instruments. The data obtained for such big number of different polar organic compounds determined using high-resolution mass spectrometry analyser gave quite new results in sensitivity and selectivity of the method. I can see an important practical aspect of the work giving the powerful tool for modern analytical laboratories determining PPCPs and similar, hazardous PPCPs in the aquatic environment. It is particularly important to me that the work relates to research in both the effluent and in the untreated wastewater. This allowed for the estimation of effectiveness of removal efficiency in wastewater treatment plants operating today in relation to commonly used pharmaceuticals.



I regard as very valuable the studying of the effect of photo degradation of PPCPs as a specific treatment to complete removal of various organic pollutants in waste waters, described detail in the scientific paper "The synergistic effect of advanced oxidation processes to eliminate resistant chemical compounds". The result of this work indicated that an AOP technique based on non-thermal atmospheric plasma discharge using photo catalytic materials is able to decompose some of very stable organic compounds in aquatic environment. Moreover, the important for me is finding that decomposition of studied compounds in such condition is strongly improved by synergistic effect of TiO₂ catalysed photo degradation, presence of oxidative radicals as well as wide range UV radiation.

I would like to point out that the experiments have been performed in an international scale. As I good understand experiments have origin from Umeå University in Sweden as well as from University of South Bohemia in České Budějovice in Czech Republic.

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**):

Elaboration level of the presented PhD thesis is very high. Main text is well organized and presented. All necessary information and data is adequate to the area of the experiment and the result discussion. The statement of objectives of the manuscript is adequate and appropriate in view of the subject matter. All results are well documented. The title of this manuscript clearly reflects its content; the abstract is sufficiently informative. All tables and figures are necessary and complete. The only caveat is presentation on the 16 pages (page 46 – 62) structural formulas of the target chemical compounds. Although this is a very image, I think it is pointless in the main text and should be included as an annex.

I want to underline, that most of the results from the experimental work are published in scientific publications of international circulation and are presented in this form in the doctoral elaboration. Simply the document is complete. English language is excellent.

Oksana Golovko, M.Sc. has studied and cited an appropriate number of scientific publications used and quoted in the thesis. It is the evidence that she is very knowledgeable about the problem discussed in the thesis.



OVERALL COMMENTARY ON THE PhD THESIS

Please write comments in extent of 1-2 pages:

First of all I want to underline that the elaboration with details describes investigated analytical problem, performed experiment and the discussion is, clearly presented and well documented.

The work is devoted to very important problem concerning the fate and stability of many of pharmaceuticals and other human used chemicals in water environment. The origin of the investigated compounds is anthropogenic. Therefore the knowledge of their distribution and stability in aquatic systems is very important to find a successful method giving a tool for decomposition of such resistant compounds during wastewater treatment.

From the work, I good know that the selectivity and sensitivity of the analytical method is excellent. Therefore, trying to explain these phenomena might be very interesting from scientific reason.

It is noteworthy that one of the strongest sides of the study is the investigation on storage effect with regard on the stability of the target compound (however, only PPCPs), what is widely discussed in this work. Especially the finding that the stability of target compounds in the sample under the storage condition should be thoroughly investigated before the analysis.

I am wonder why the temperature of -18 °C causes such sever degradation of the analyte. It is not explained in the thesis.

It should be emphasized that in many analytical activities the target compound loss in the sample caused by many chemical/biological and physical processed is not recognized yet or simply not taken into account at all!

Author reports (Chemosphere 111, 2014, 55-60) that 30 test compounds were unstable in the treated wastewater, while 51 were unstable in untreated wastewater. But the problem is not discussed why?

However, it is very important to know which compound is unstable and prone to decomposition in wastewater treatment process. This may be an indication for the selection of appropriate wastewater treatment technologies.

I must clearly emphasize the great importance for the study of what are the results of studies on the photo degradation of many pharmaceuticals in the aquatic environment. Particularly an indication of which of the investigated compounds are rapidly decomposed, and which are resistant to experiments conducted with respect to their degradation.

In table 2 on page 64 the author of the work presented half-lives for selected PPCPs studied by the other researchers. Quoted data are, however, in many cases, from the aquatic environment modified with buffers or organic solvents. It is difficult, therefore, to refer to these results, as the author of the work done research in pure water. Therefore, this comparison may not be appropriate.

Minor:

On the page 63 there is the statement that: "The data about weather conditions is available on <http://www.tfe.umu.se/weatherold/csv.html>"

Information is difficult to access and is in Swedish.

"All samples were stored in the dark (wrapped in aluminium foil) and cold (4°C) before and after exposure." As it is concluded from the investigation on storage conditions time of the storage of



samples before analysis is critical. There is no information how long samples were stored before analysis.

Appreciating the huge scope of the experimental and analytical work, I cannot make any reservations about the scope of the experiment, but there is one suggestion for future experiments – it might be useful to explore the area of the target compound decomposition pathways.

It is interesting, because the author showed the presence of certain compounds in the treated wastewater, and the lack of it was untreated wastewater.

I would like to point out that the data obtained in the study can be priceless in supplementing and corroborating the factors for the calculation of the degree of degradation of PPCPs in wastewater treatment plants and the search for new methods of biological and physico-chemical decomposition.

The work is an important scientific report and is a novel solution both in terms of a scientific experiment, and the interpretation of the obtained results. In my view, the study should be continued.

I want to indicate that I determine Oksana Golovko's Doctor of Philosophy thesis outstanding. Therefore, I would like to express my very good opinion about the thesis submitted for the review and with full confidence I bring to the Faculty Council for admission to further stages of dissertation defense.

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

K. P. Hlaváček, P. Olsáček
24th of July 2019
.....
Date and place

Adam Groboudik
.....
Name and signature