



# Politechnika Łódzka

Wydział Inżynierii Procesowej i Ochrony Środowiska

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## Review

of the Doctoral Dissertation by Humam Ahmed  
entitled „Degradation of selected drug used in COVID-19 therapy in the aquatic  
environment by means of solar light driven processes”  
conducted in the Department of Environmental Biotechnology, Faculty of  
Energy and Environmental Engineering, Silesian University of Technology  
under the supervision of Prof. D. Sc. Eng. Ewa Felis

### Basic information

The doctoral programme was conducted in accordance with the Act of 20 July 2018 Law on Higher Education and Science (Journal of Laws 2024, item 1571, as amended) in the field of engineering and technical sciences in the discipline of Environmental Engineering, Mining and Power Engineering.

The evaluation of the doctoral dissertation was based on the decision of Discipline Council for Environmental Engineering, Mining and Power Engineering at the Silesian University of Technology made at the meeting on December 18, 2025. The dissertation was submitted to me for review on January 19, 2026.

### General information

The dissertation concerns the solar light driven degradation of several antiviral drugs such as isoprinosine, ritonavir and remdesivir. The study investigated direct photolysis, photocatalytic processes and H<sub>2</sub>O<sub>2</sub>-assisted photolysis under simulated solar irradiation. The investigations address an important problem of the degradation paths of the compounds used during the COVID-19 pandemic. On the one hand it may help to predict their fate in the environment (due to the solar light penetration in water bodies), on the

other enable the development of the effective wastewater treatment – removal of the tested pollutants.

### **Originality and significance of the dissertation topic**

The study systematically evaluates the direct photolysis and photocatalysis under solar light irradiation in three water matrices (milliq-Q water, tap water and water from the Ostropka river) providing new environmental data on their stability and transformation behaviour. Some insights into the degradation mechanisms and kinetics were also obtained.

First, it was observed that simple solar photolysis is inefficient in these drugs degradation what confirms their high photostability. The presence of salts, ions and organic matter was shown to influence the drugs degradation. The usage of various photocatalysts caused significant improvement in the degradation efficiency of Isoprinosine, while the ritonavir and remdesivir were adsorbed on the photocatalysts. The addition of hydrogen peroxide to solar light photolysis resulted in the complete decomposition of isoprinosine and ritonavir. At the same H<sub>2</sub>O<sub>2</sub> doses remdesivir was degraded by more than 80%. The experiment conducted under dark conditions by the highest hydrogen peroxide dose used (in the “light” conditions) confirmed that the mechanism involved hydroxyl radicals’ generation. In the case of the isoprinosine photocatalytic degradation the influence of the ions such as sulphate, chloride, nitrate and carbonate was evaluated.

Although there are some literature data concerning the above-mentioned drugs photodegradation, there is no so comprehensive investigations on the solar light driven processes.

### **Dissertation structure and editing**

The doctoral dissertation is a 132-page manuscript containing 25 figures, 18 tables and an additional 16 figures attached in the Supporting Information. The dissertation structure is correct. It is divided into the following chapters: 1. Literature review, 2. Research hypothesis, purpose and scope of thesis, 3. Materials and Methodology, 4. Results and Discussion, 5. Summary and Conclusion, 6. Future Research Direction, 7. References, 8. Supporting Information, 9. List of Figures, 10. List of Tables, 11. List of Publications and 12. List of other scientific activities.

The dissertation is generally well prepared, however there are some editorial shortcomings. Acronyms are not listed in the alphabetical order what hinders using it. There is a lack of a reference to a literature source regarding the properties of Isoprinosine (Table 2. Page 25). Equation (1) has incorrect dot between the constant of pseudo-first-order kinetic rate ( $k_t$ ) and time ( $t$ , page 43). Surprisingly, chapter 4 has the same name as subchapter 4.1. (Results and discussion). Many figures are divided into a), b) and c) – in my opinion they should be numerated as separate figures. Although the whole dissertation is written in a very good English, there is an error in the term “cumulative” in figures 9 – 11, 17, 20-21. What is more, the unit of the cumulative energy is wrongly written – KJ/L. It should be kJ/L. Figure 17 (page 70) showing the results of

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dark sorption experiments has also “Cumulative energy” on the OX axis instead of reaction time.

### **Substantive value of the dissertation**

The doctorate candidate begins the dissertation with a short Introduction to the topic (subchapter 1.1). Next, she describes antiviral drugs as emerging pollutants (1.2), emphasizing their behaviour and fate in the aquatic environment. Furthermore, advanced oxidation processes (AOPs) are discussed as a technique for removing anthropogenic contaminants (1.3), with the insight to AOPs mechanisms (1.4). In subchapter 1.3. there is a repetition of the information already contained in subchapter 1.2 – namely about the presence in and harmfulness to the aquatic environment of the studied pharmaceuticals. Apparently, the AOPs mechanisms are not very deeply described. What is more, there is lack of their kinetic models outline. Following subchapters are devoted to environmental benefits (1.5), disadvantages (1.6), mitigation strategies for the latter (1.7) and sustainable development goals impacted by AOPs (1.8). In my opinion, the negative impact of AOPs on the environment and the possibilities for its mitigation are very well described. The last chapters include a detailed description of the drugs used in the study (1.9). The thesis is based on 124 literature sources, of which 84 were published in the last five years.

Chapter 2 clearly formulates the research hypothesis, purpose and scope of the dissertation. In fact, the literature review (Chapter 1) does not contain information regarding the influence of the type of photocatalyst, the composition of the aqueous matrix, or the operational parameters on solar light driven photocatalysis, so I have doubts if the research hypothesis (2.1) is based on this review. The same drawback applies the scientific problems that are presented in Chapter 2. Subchapter 2.3 presents the main goal of the study. In my opinion it is stated too broadly as the dissertation does not contain results from the investigations performed both under sunlight and artificial light exposure – only artificial one. Specific aims and objectives of the study shown in the subchapter 2.4 are more precise – I have not found only the investigations concerning the influence of the pollutant concentration on the process efficiency. Subchapter 2.5 shows the scope of the thesis.

Chapter 3 well describes the materials and methodology used within this study. Generally, used methods are precisely characterised. However, the description of the procedures might have been shortened – e.g. in subchapter 3.3.5 concerning photolytic studies, the method of conducting the process is presented separately for each of the drugs. The same applies to research on the photocatalysis process (subchapter 3.3.6). The results of the investigations were presented in tables and figures, described and partially discussed with the literature data in Chapter 4. First, the results of the ion profiling of the water matrixes used are described (4.1.1). I do not understand why the doctorate candidate did not show (Table 6.) the amounts of the ions – she had chromatograms and the calibration of the ion chromatograph was mentioned in the Chapter 3. It is obvious that milli-Q water, tap water and surface water differ in the ion's

concentrations. The statement that it was one kick or three kicks (Table 6.) of the specific ions is highly insufficient.

The photolytic degradation of drugs used in this study was analysed in subchapter 4.1.2. It was observed that higher removals were obtained in surface water than in Milli-Q water, while the author discussed in this chapter literature results with the conclusion that surface water matrix might reduce photolysis efficiency. It does not match her results. Generally, this subchapter was closed with the right conclusion that investigated drugs are not effectively degraded in photolysis process under artificial solar light irradiation. Despite the low degradation rates, the author tried to fit pseudo-first order kinetic to the obtained photolysis results. The title of Table 7 is thought-provoking – what does it mean “first-order pseudo constants”?

Next subchapter (4.1.3) shows the photocatalytic degradation of selected drugs by different photocatalysts.  $\text{TiO}_2$  and  $\text{ZnO}$  led to complete removal of Isoprinosine when used in the doses of 5 and 10 mg/L. It would be advisable to show the fit to pseudo-first-order kinetics on the graphs – not only in tables. It is hard to follow the kinetic of ritonavir and remdesivir degradation under photocatalytic conditions as the doctorate candidate shows only curves concerning the adsorption process of both drugs. Those curves for ritonavir confirm that adsorption process followed the proposed model – Langmuir isotherm. In contradiction, Figures 14 and 16 disprove the assumption that the adsorption process of remdesivir proceeds according to the proposed adsorption-desorption model – fitted curve (Model\_⊖) has totally different trend than experimental data (EXP\_⊖).

The results of the investigations on photolysis assisted with hydrogen peroxide were presented in subchapter 4.1.5. It is underlined that hydrogen peroxide addition to photolysis process led to the significant improvement in the degradation efficiency of all drugs. The author did not link the results obtained in dark conditions to the hydroxyl radicals' occurrence in light conditions in the presence of hydrogen peroxide.

Subchapter 4.1.6 shows the effect of single ions (sulphates, chlorides, nitrates and carbonates) on the photocatalysis of Isoprinosine. What is very valuable in this part of the dissertation is an attempt to explain the mechanisms of those ions influence on the photocatalytic process.

Subchapter 4.1.7 could be omitted. It is devoted to the ions influence on the ritonavir adsorption. First, there are not enough data to draw any conclusions. Secondly, the adsorption process itself is not a most important aspect of the dissertation. Thirdly, there is no information in what conditions (dark or light) was the adsorption process conducted.

The mineralization of organic matter, described in subchapter 4.1.8, is doubtful. It is also a part of this work, that could be omitted.

Chapter 5 presents key contributions of the research (as seen by the author), conclusions and novelty statement. I can agree that:

1. It is a first comparative study on the solar degradation of remdesivir, ritonavir and Isoprinosine,

2. The study demonstrated that photolysis alone is insufficient in the above mentioned drugs degradation,
3. Various photocatalysts improved the degradation efficiency of these drugs,
4. Experiments conducted in different water matrixes provided a realistic assessment of specific ions and overall salts and organic matter content influence on the photocatalysis process,
5. The degradation kinetics were modelled using pseudo-first order reaction for photodegradation and Langmuir-Hinshelwood equation for the adsorption of ritonavir.

The other “contributions” are not enough confirmed within this dissertation.

Generally, the conclusions are an elaborate description of the key contributions. Among the novelty statement there are some expressions that in my opinion are not proved by this dissertation. There are listed in the next section of this review (questions 15 to 18) – as a base for the discussion with the doctorate candidate.

Chapter 6 is a valuable part of the dissertation – drawing plans for the future works on the solar photolysis and photocatalysis of the selected pharmaceuticals.

#### Critical comments requiring clarification and issues for discussion

1. Page 39, subchapter 3.3.5.1: What does it mean: “Aliquots were collected at predetermined time intervals (...), and 120 minutes, **both before and after irradiation**”?
2. Page 42, subchapter 3.3.9: How was it possible to prepare such a high concentration like 500 mg/L of ritonavir and remdesivir that are slightly soluble in water?
3. Page 44, subchapter 4.1.2: What other mechanisms might have caused that the degradation efficiency in surface water was higher than for ultra-pure water?
4. Page 58, Subchapter 4.1.3.1: How is it possible that degradation rate of Isoprinosine in surface water was 23%, while on the Figure 11c.  $C/C_0$  is close to 0.4?
5. Pages 59-65: Why was the adsorption process evaluated under solar radiation?
6. Page 63, subchapter 4.1.3.3.: Please explain the sentence: “The  $TiO_2$  P25 system demonstrated a slightly higher overall adsorption percentage (99,21%) compared to ZnO (100%)”
7. Please explain figures 14a and 14b.  $EXP_{\ominus}$  shows completely different trend than  $Model_{\ominus}$ . How is it possible that correlation coefficient is 0.861? How the doctorate candidate calculated the coefficient of determination for this fitting? Please, show the formula and exemplary calculations.
8. Subchapters 4.1.3 and 4.1.4: What was the difference between adsorption process under light and dark conditions of ritonavir and remdesivir?
9. Page 74, subchapter 4.1.5: Why the doctorate candidate claims that 100% degradation of Isoprinosine by  $H_2O_2$  dose equal to 500  $\mu$ L lasted 120 minutes?

10. Page 77, subchapter 4.1.5: What does it mean “pseudo drug degradation kinetic”?
11. Page 78, Subchapter 4.1.6.1: How were the degradation rates of Isoprinosine calculated, if the drugs’ concentration was below detection limits?
12. Page 83, subchapter 4.1.6.3: Please, explain equation 16 – what are the substrates and products in this equation?
13. “This work determined (...) main products of photodegradation” What products were determined?
14. “This was the first study (...) with a focus on real-world application”. In what way was the research focused on real-world application?
15. “The study on ritonavir and the evaluation of the percentage removal of remdesivir using a two-phase kinetic model based on a unique adsorption-desorption dynamic represented a novel contribution to this filed”. Where was the ritonavir linked to this model? Question 7. already addressed the problems with the modelling of the remdesivir adsorption process by this model.
16. On what base the doctorate candidate stated that the solar light driven processes are scalable? Were any experiments in different scale performed within this study?

#### **Final assessment of the doctoral dissertation**

To sum up – the doctoral dissertation of M. Sc. Humam Ahmed is of sufficient substantive value and provides some (listed above as a key contributions) new and interesting information on the solar light driven processes used for the degradation of the three antiviral drugs: isoprinosine, ritonavir and remdesivir. Although some of the results and conclusions should be re-examined and discussed, the doctoral dissertation submitted for the review is an original contribution to the field of the environmental engineering, mining and power engineering. Furthermore, the dissertation proves that M. Sc. Humam Ahmed has theoretical and practical knowledge in the solar light driven processes.

The doctoral dissertation submitted for review, entitled “Degradation of selected drugs used in COVID-19 therapy in the aquatic environment by means of solar light driven processes” meets the formal requirements for doctoral dissertations specified in the Act on Higher Education and Science of July 20, 2018. Therefore, I appeal that the Discipline Council for Environmental Engineering, Mining and Power Engineering at the Silesian University of Technology admit M. Sc. Humam Ahmed, to the next stages of the doctoral procedure.

Podpisała Katarzyna Paździor