Lodz University of Technology
Institute of Applied Radiation Chemistry

Review Report on the PhD Thesis

Radiation-Induced Degradation of Selected Chlorinated Emerging Organic Pollutants in Aqueous Solution Under Electron Beam Irradiation

authored by Stephen Kabasa

submitted to the scientific committee of the Institute of Nuclear Chemistry and Technology for the award of Doctoral degree in natural sciences in the discipline of chemical sciences

Wastewater treatment has become an inevitable problem due to population growth, urbanization and the effects of climate change. Wastewater treatment generally involves three stages, called primary, secondary and tertiary treatment. Primary treatment consists of removing settled and floating materials by holding the sewage in a basin. Pre-treated sewage is a complex aqueous solution of different characteristics. The further treatment requires advanced technologies depending on the wastewater composition. Particularly challenging is removal of harmful microorganisms and dissolved hazardous chemicals, such as pharmaceutically active compounds. The application of Electron Beam (EB) technology to purification of wastewater from hazardous organic pollutants is the subject of research conducted at the Institute of Nuclear Chemistry and Technology (IChTJ) headed by Prof. Andrzej Chmielewski. Mr. Kabasa's PhD studies, supervised by Dr, Yongxia Sun (Professor IChTJ), and the submitted dissertation deal with these problems. Chloroquine (CQ) and hydroxychloroquine (HCQ) are derivatives of quinoline commonly used in antimalarials with potential application in the treatment of rheumatoid diseases. Their use is, however, associated with the release of halogenated organic compounds into wastewater increasing environmental accumulation of the toxic chemicals. Developing technologies that effectively remove chlorinated organic pollutants is important and also challenging. Thus,

the topic of the thesis is up-to-date and relevant to the discipline of chemical sciences.

The dissertation is written in English, except for Streszczenie which is written in Polish. The manuscript includes Dedication, Acknowledgments, English Abstract, Streszczenie, Contents, List of **39** Figures, List of **6** Tables, Abbreviation, 5 Chapters covering **148** pages, Bibliography

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including **237** references, and **12** Appendices. *Chapter One* presents a brief introduction to the topic, motivations, and objectives. *Chapter Two* reviews wastewater treatment technologies and provides basic information on water radiolysis. *Chapter Three* describes methodology. Results of the conducted experiments and numerical simulations are presented and discussed in *Chapter Four*. *Chapter Five* contains conclusions.

The literature is very rich and carefully prepared. The bibliography items are correctly selected. It is worth emphasising that Mr. Kabasa used the latest literature on the subject. Most of the cited publications were issued in the last 5-6 years. It shows the growing interest in the use of radiation technologies for wastewater treatment.

The research objective defined by the PhD Candidate included experimental studies and numerical simulation of EB-assisted degradation of CQ and HCQ depending on their concentrations and the applied radiation dose in different chemical environments. The influence of the chemical environment on the removal efficiency was determined in several research tasks including: conditions prompting generation of the hydroxyl radical (•OH), the hydrogen radical (H•), and the hydrated electron (e_{aq}^-), aerated solutions, solutions with variable initial pH, and the presence of additives such as inorganic ions, humic acid, the hydrogen peroxide (H_2O_2), and the catalysts TiO_2 and g-C_3N_4. Mr. Kabasa assessed removal efficiency by measuring changes in concentration of CQ and HCQ. In addition, he monitored the degradation by-products under EB and EB-Fenton assisted treatments of initially neutral solutions containing 125 mg/L of the investigated compounds. The solutions were irradiated at the dose ranging from 0.5 to 7 kGy. To evaluate the effectiveness of CQ and HCQ removal he also used COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon) parameters and measured nitrogen content in solution. Based on analysis of several by-products he proposed a mechanism of CQ and HCQ degradation under EB treatment. Mr. Kabasa used UV spectroscopy, HPLC analysis, LC-MS, and colorimetric methods to carry out the experimental part of his work. **This proves the PhD Candidate's ability to use a variety of experimental techniques to achieve his research goals.**

The experiments conducted by Mr. Kabasa showed that CQ and HCQ can be effectively degraded into less toxic compounds under the EB treatment, but their mineralization is incomplete.

Before evaluation of the simulation part of the thesis I have the following questions to the Author:

1. How do you define the removal efficiency, by eqs. (3.25) or by (4.11)? Fig. 4-3 is also confusing.
2. Most of the experiments were done for the highest solute concentration of 125 mg/L. How this value compares with the typical content of chlorinated organic pollutants in wastewater?
3. How do you explain the decrease in removal efficiency observed with increasing concentration of solutes?
4. Based on your expertise, what actions (parameters) should be taken into account to optimize the removal of quinoline derivatives in wastewater treatment using EB technology.

Evaluation of the simulation part of the thesis

Mr. Kabasa performed numerical simulation using the CHEMSIMUL software package. The description of the computational procedure presented in Section 3.7 is very short and not precise. On p. 76 we read: "The concentration of species i (C_i) in the solution at any time (t) is described by the following ordinary differential equation …(3.26), where r_i is the rate of formation of species i per unit volume." Questions: *i*) what species do you mean?; *ii*) what is the concentration unit; *iii*) what are the values of r_i ?

Further we read: "Equations derived for each species are presented as ordinary differential equations and numerically solved …. to describe the change in concentrations of each species with respect to time….. Additionally, pH was varied between 2 and 12 to show the effect of pH on the degradation process" Questions: *i*) are we talking about the same species as in eq. (3.26); *ii*) how these equations were derived; *iii*) how was the change in pH modeled ?

The description of simulation results is given in Section 4.8. On p. 122 one can read "Models describing the data on the formation of stable products of water radiolysis, H_2O_2, O_2, and H_2, were reported in several publications (Jenks, 1965; Jenks and Griess, 1967; Boyd et al., 1980; Burns et al., 1983)", but the mentioned references were not included in the bibliography.

Further we read: "For simulation, 110 reactions (Appendix 4) based on radiolysis of aqueous systems were used to simulate the degradation of CQ and HCQ solutions under EB irradiation" Question: was the same set of 110 reactions assumed for all the systems studied?

Appendix 4 presents set of reactions along with the second order rate constants (in $M^{-1}s^{-1}$).

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In this reaction set I didn't find the diffusion controlled reaction: ($e^-_{aq} + e^-_{aq} = H_2 + 2OH^-$). Instead, I noticed order of magnitude errors in the values of reaction rate constants. To list some of the most critical:

$k(H_2O = H^+ + OH^-)$ is 1.4E01 instead of $2.6 \cdot 10^{-5}$;

$k(H_2O_2 = H_2O + O)$ = 1.00E-03 instead of $7.3 \cdot 10^{-8}$;

$k(H + H_2O = H_2 + OH)$ = 1.1E01 instead of $3.5 \cdot 10^{-4}$;

$k(HO_2^- + H_2O = H_2O_2 + OH^-)$ = 1.17E01 instead of $1.0 \cdot 10^5$

Moreover, k(2*OH) = 3.6E10 but on p. 74 is $6 \cdot 10^9$.

For the reasons mentioned above I am not satisfied with the computational part of the thesis. In my opinion, the results of the numerical simulations are not reliable. I recommend to carefully re-analysed the input data. Moreover, to minimize numerical errors, set of input reactions should be consistent with the investigated conditions.

<u>The most important editorial shortcomings are listed below:</u>

- At several places narration is chaotic, and statements are not clear or misleading. In particular, on p. 75: is ΔC a pollutant concentration or rather its change due to absorbed dose?; in eq. (3.25) if ΔC is expressed in mol/L why the conversion of Gy to 100 eV/L is used; below eq. 2.3 units of concentration and D are not given.
- Captions to the figures are not precise. Example 1: Fig. 4-3 shows: (parts a and b) removal efficiency (of what CQ or HCQ?) versus dose; (parts b and e) the dependence of the rate constant k in kGy^{-1} (of what CQ or HCQ) on concentration in mM; whereas parts (c) and (f) show the product kD as a function of dose. Example 2: In caption to Fig. 4-4 symbol k is defined as a dose constant, whereas on p. 84 as a rate constant, etc.
- There are unnecessary repetitions of the same content throughout the manuscript. I also noticed that references Ponomarev 2020a and Ponomarev 2020b are the same.
- Translation of Abstract into Streszczenie could be better if the Author ask Polish colleagues for help.
- Finally, it's a pity that the Author did not listed his scientific achievements.

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Despite the above criticism the essential scientific value of the thesis is good and my opinion about the research work done by the PhD Candidate is positive. Mr. Kabasa has appropriate knowledge of the subject, and ability of using various experimental techniques and physicochemical measurements to achieve his research objectives.

According to Scopus, he is the co-author of three articles published in NUKLEONIKA [*Computer-simulated degradation of CF_3Cl, CF_2Cl_2, and $CFCl_3$ under electron beam irradiation* 2023;68(3):67-76; *Degradation of hydroxychloroquine in aqueous solutions under electron beam treatment* 2024;69(2):53-63; *Chloroquine degradation in aqueous solution under electron beam irradiation* 2024;69(2):65-74]. Although, the latter two papers relate to the issues discussed in the thesis, they were not cited in the dissertation.

In conclusion, taking into account novelty elements, the extent of the work, and significance of the results the reviewed doctoral dissertation meets the requirements of The Act of July 20, 2018, Higher Education Law and Science (with later amendments). Mr. Stephen Kabasa proved to have the ability to conduct scientific research. Therefore, I am applying for admission to public defence.

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