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REVIEW

of the Ph.D. thesis of Stephen Ochieng Kabasa entitled

"Radiation-induced degradation of selected chlorinated emerging organic pollutants in aqueous solution under electron beam irradiation"

The Ph.D. thesis of Mr. Stephan Kabasa, presented to me for review by the Scientific Council of the Institute of Nuclear Chemistry and Technology in Warsaw was carried out under the supervision of D. Sc. Yongxia Sun, prof. IChTJ. The topic of the thesis is current, has a strong cognitive aspect and refers to global concerns about the pollution of water resources and the search for new, effective methods of their purification, which is of key importance for the functioning of modern society.

The thesis of Mr. S. Kabasa concerns the radical reactions of chloroquine and hydroxychloroquine, which belong to halogenated quinoline derivatives, and falls within the scope of research carried out in the group of Prof. Sun. Halogenated organic compounds are often used in pesticides, solvents, pharmaceutical products, among others. Many of them are known to be stable, bioaccumulative, toxic, mutagenic, carcinogenic. They have been detected in surface water, groundwater, and wastewater. These pollutants are rarely regulated in water and sewage treatment, especially in the discharge of domestic wastewater, and therefore are released into aquatic ecosystems. Conventional methods are not sufficient to remove this type of pollution. Therefore, there is a need to search for effective technologies of water and wastewater treatment.

For this reason, Mr. S. Kabasa decided to investigate the effectiveness of radiation methods in the process of removing organic contamination in the aqueous phase using model compounds chloroquine and hydroxychloroquine.

The Ph.D. dissertation comprises 186 pages. Its layout is typical and corresponds to the generally adopted presentation scheme of scientific works. The thesis consists of five main chapters: *Introduction* (17 pages), *Literature review* (43 pages), *Methodology* (21 pages), *Results and Discussion* (65 pages), and *Conclusion* (4 pages). The chapters are preceded by an Abstract written in English and Polish, a List of Figures, a List of Tables and a very helpful list of Abbreviations. The thesis ends with Bibliography and Appendices. In total, the thesis contains 39 figures, 6 tables, 12 appendices, and 280 literature positions. It should be emphasised that the cited papers are in the vast majority published in the last few years, which shows that the Author has a very good knowledge of the current literature on the subject.

Chapter 1 *Introduction* contains basic information about various types of pollutants occurring in the aquatic environment, information about their persistence, toxicity, mutagenic and carcinogenic properties. As well as information about the effectiveness of radiation techniques as methods of water and wastewater treatment for a wide range of organic and inorganic pollutants. In this chapter the Author clearly specifies the scope of the work and the objectives regarding: (i) the degradation of chloroquine and hydroxychloroquine upon electron beam irradiation, (ii) the identification of the degradation products of chloroquine and hydroxychloroquine, (iii) the influence of different parameters such as dose, dose rate, pH of the solution, presence of anions and so on, on the degradation efficiency of the investigated compounds, and (iv) the development of numerical simulations of chloroquine and hydroxychloroquine degradation in order to understand the degradation mechanisms.

The literature part (chapter 2) presents the characteristics and effectiveness of various water treatment methods used to obtain the desired quality of drinking water or discharged wastewater. These methods include coagulation combined with flocculation, sedimentation, filtration and disinfection (on which the conventional surface water treatment plants are based), biological treatment methods, adsorption and ion exchange

method, membrane techniques, techniques based on chemical and electrochemical oxidation.

The most important part of this chapter is the description of the possibilities of using ionizing radiation in the process of water purification, both electromagnetic and particle radiation, including fast electrons with energy in the range of MeV. The Author discusses the process of water radiolysis, dividing it into physical, physicochemical and chemical stages. In particular, he discusses the reactions of products generated in this process, including reactions with solvated electrons, hydrogen atoms, molecular hydrogen, perhydroxyl radicals, and hydroxyl radicals. Due to the fact that electrons and hydroxyl radicals are produced with the highest efficiency and are the most reactive species, these products and their reactions are discussed in the most in-depth way. In the following, the Author compares the possibilities of using gamma radiation and fast electron flux, taking into account their properties, available sources, safety features and economic issues. He discusses, based on the available literature, the possibilities of degrading different types of drugs and the efficiency of these processes under different conditions with respect to dose, pH, addition of H_2O_2, humic acids and inorganic ions.

In chapter 3 the experimental procedures are described. Subchapter 3.1 contains a list of chemical compounds and solvents used during the studies. In subchapter 3.2, the Author describes the analytical techniques applied. In particular, he discusses the following techniques: HPLC, LC-MS, UV spectrophotometry, calorimetric methods, and the pulsed radiolysis method using a linear electron accelerator LAE 10, which has been successfully used for many years to monitor the transformations of short-lived radical products. The Author also discusses the application of mathematical modelling of radiation-induced degradation of chloroquine and hydroxychloroquine as well as the use of QSARs and ECOSAR programs for ecotoxicity analysis. In this chapter the Author discusses the reduction of Cr(VI) by hydrogen atoms ($H^{\bullet}$) and hydrogen peroxide (H_2O_2) and its re-oxidation by OH (page 74): in the text he claims that the reduction leads to Cr(III), while in reactions 3.18 and 3.20 he takes into account Cr(V) – please comment on this. For consistency, the Author should use Cr(VI)/Cr(V) or Cr^{6+}/Cr^{5+}.

Results and their discussion are presented in chapter 4, which is the most comprehensive chapter of the thesis, in which very rich experimental material has been collected. In the first stage, the Author examined the reactions of OH, H and e_{aq}^-, generated during the radiolysis of water, with chloroquine and hydroxychloroquine and the effect of radiation dose on the degradation process. The results of the studies showed that the removal efficiency of chloroquine and hydroxychloroquine was higher under the OH conditions than under e_{aq}^-. At the same time, the removal efficiency of both compounds was higher in the case of their reactions with the H radicals than with e_{aq}^-, and lower than with OH radicals. Surprisingly, as shown in Fig. 4-2 the removal efficiency of chloroquine and hydroxychloroquine was pretty the same in aerated and oxygen-free solutions. At this point I have a question for the PhD student: how should the results shown in Fig. 4-2B (such data are missing in Fig. 4-2A) and labelled EB be interpreted? In addition, on page 86 the Author states: *"However, according to the reactions in Fig. 4-3 in N_2O saturated solutions containing 0.5M tert-butanol in pH < 2, H˙ had higher removal efficiency compared to e_{aq}^- for both CO and HCQ removal"* – Fig. 4-3 shows the effect of initial CQ and HCQ concentration on removal efficiency, so please explain how to read this statement.

In the next stage, the Author carried out a series of studies concerning the effect of initial concentration of pollutants on their degradation efficiency. These results led to the conclusion that the removal efficiency decreases with increasing concentrations of chloroquine and hydroxychloroquine at the same absorbed dose. In general, for all pollutant concentrations at doses above 2 kGy, the degradation efficiency was about 70-80%. This efficiency increased to 90 and 99% for hydroxychloroquine and chloroquine, respectively, at the lowest concentration and dose of 7 kGy. The same trend was observed for the pollutant degradation reaction rate coefficients as a function of pollutant concentration at a constant radiation dose. The k values decreased with increasing pollutant concentrations, at the same time the k values were higher for the chloroquine degradation reaction than for hydroxychloroquine. In addition, the Author investigated the effect of pH, inorganic ions, humic acids, and hydrogen peroxide on the removal efficiency of both pollutants obtaining a very valuable results.

Of high importance are the results obtained for the degradation reaction under the conditions of electron beam coupled with catalytic oxidation. The studies were carried out by combining EB treatment of the aqueous solutions with Fenton oxidation or the use of catalysts, i.e. TiO_2 and g-C_3N_4. As observed during Fenton-assisted EB, the highest removal efficiency of 90 and 94% for chloroquine and hydroxychloroquine, respectively, was obtained for a H_2O_2:Fe^{2+} molar ratio of 20. At the same time, the removal efficiency of chloroquine was higher than that of hydroxychloroquine at the respective molar ratios and Fenton reagent concentrations. Under conditions of electron beam coupled with catalyst the effect was negligible or negative. It should be noted here that this section of the thesis has not been presented in a clear and legible manner. For instance, the Author moves from discussing the Fenton reaction to the Fenton-assisted electron beam and then back to the Fenton reaction, which is misleading. On page 99 (a similar statement was made on page 101) the Author states: *"Similarly, when the peroxide proportion was much higher (10x and 20x), the removal efficiency for CQ and HCQ was suppressed"* – there is some inconsistency between the removal efficiency values discussed in the text and those presented in Fig. 4-7 for HCQ. I would like to ask the Author to comment on this.

The experimental results are clearly summarized in the chapter *Conclusions*. In my opinion, the most important achievements of the PhD student include:

1) demonstration that the initial concentration of pollutants affects the efficiency of their degradation,
2) demonstration that both the OH radical and e_{aq}^- play a substantial role in the degradation of chloroquine and hydroxychloroquine. However, the contribution of OH to the degradation efficiency of both pollutants was higher compared to e_{aq}^-,
3) demonstration that the presence of inorganic ions, humic acids, and H_2O_2 suppresses the degradation of pollutants. The only exception is $S_2O_8^{2-}$, which reacts with e_{aq}^- to form strongly oxidizing $SO_4^{\bullet-}$. Hence, it was observed that an increase in the concentration of $S_2O_8^{2-}$ increases the removal efficiency,

4) demonstration that the Fenton-assisted electron beam process improves the removal efficiency of pollutants. However, the molar ratio of Fenton reagents is a key parameter that determines the process efficiency,
5) demonstration that the degradation of pollutants under EB and Fenton-assisted EB conditions does not lead to complete mineralization, which is evident from insignificant reduction of COD and TOC,
6) identification of several by-products generated from the radiation-induced degradation of pollutants,
7) prediction of the mechanism of pollutant degradation under EB and Fenton-assisted EB conditions.

As a reviewer, I have to mention minor errors, editorial shortcomings and incorrect wording found in the text, which do not affect the substantive value of the dissertation and my positive assessment:

page 10, „..*radicals that form during water irradiation*.." → „..*radicals that are formed during water irradiation*.."

page 10 and 57 „..*in the range (6 – 8)·10^{9} M^{-1}s^{-1} range where*.." → „..*in the range (6 – 8)·10^{9} M^{-1}s^{-1} where*.."

page 10, „..*gives smaller rate coefficients*.." → „..*gives lower values of rate coefficients*.."

page 20, „..*removal of chemical demand*.." → unfortunate wording

page 33, „..*Medium energy accelerators capable of producing electron energies ranging*.." → „.. *Medium energy accelerators capable of producing electrons with energies ranging*.."

page 38, „..*molecular yield g(H$_2$O$_2$)*.." → „..*molecular yield G(H$_2$O$_2$)*.."

page 41, „..when organic *molecules contain substituent halogen atoms*.." → „..*when organic molecules contain halogen atoms as substituents*.."

page 42, „..*In strongly acid media*.." → „..*In a strongly acidic environment*.." – similar wording is found in other parts of the text

page 43, „..*The H atom reacts faster with O$_2$ than with H$_2$O$_2$ (Eq. (2.27) to Eq. (2.30))*.." → „.. *The H atom reacts faster with O$_2$ than with H$_2$O$_2$ (Eq. (2.28) and Eq. (2.30))*.."

page 49, „..*mefenamic acid and ketoprofen have decomposed..*" → „..*mefenamic acid and ketoprofen have been decomposed..*"

page 56, „..*dissociative capture of* e_aq^-.." → „.. *dissociative capture of* e_{aq}^-.."

page 62, „..*electron spray ionization..*" → „.. *electrospray ionization..*"

page 66, „..*cuvettes were left to cool and the change...*" → „.. „..*cuvettes were left to cool down and the change..*"

page 66, „..*Thus, it is removed from the unwanted oxidation to elemental chlorine. Silver sulfate catalyzes to increase the oxidizability of aliphatic substances. Therefore, lower apparent findings are avoided...*" → What does the Author mean here?

page 70, „..*Where q is the charge of the particle charge..*" → „..*Where q is the charge of the particle..*"

page 78, „..*ECOSAR is a free computer program used by..*" → *sentence was not completed*

page 80, 81 – Lack of literature references in table 4.1 and figure 4.1.

page 83, „..The *removal efficiency for CQ and HCQ was higher in the OH conditions..*" → „.. The *removal efficiency of CQ and HCQ was higher under the OH conditions..*"

page 87, „..*much slower rate..*" → „.. *much lower rate..*"

page 87, „..*was comparatively like CQ..*" → „..*was comparable to CQ..*"

page 88, The descriptions inside Fig. 4-4 d are illegible.

page 121, Lack of consistency in using BOD. One time its biochemical oxygen demand another time biological oxygen demand.

page 123, „..*the OH molecule..*" → „..*the OH radical..*"

page 133, „..*at m/z = 370, 158, 159, 279, and 292 (Fig. 4-27 A, B,..*" → „..*at m/z 370, 158, 159, 279, and 292 (Fig. 4-28 A, B,..*"

page 135, „..*the alky side..*" → „.. *the alkyl side..*"

In many places in the thesis the Author used *rate constant* instead of *rate coefficient*. In addition, there are many repetitions in the thesis, especially in relation to the products of water radiolysis. The list of abbreviations is missing many of the acronyms used in the work. In many places, there are missing spaces.

Despite of some critical comments, Mr. S. Kabasa has met the intended research objectives with interesting and valuable results and thereby has proven that he is capable of solving research problems. Mr. Stephen Kabasa, according to Web of Science Core Collection, is a co-author of 4 publications, one of which was published in 2023 (in the journal *Nukleonika*) and the other 3 in 2024 (two papers published in *Nukleonika* and one in *Processes*). Three of these publications are related to the topic of his Ph.D. thesis. The total impact factor of the publications is 4.9.

In view of the above, I conclude that the doctoral dissertation of Stephen Ochieng Kabasa entitled "Radiation-induced degradation of selected chlorinated emerging organic pollutants in aqueous solution under electron beam irradiation" fulfils all the requirements provided for in the Polish act on scientific degrees and academic title (*Ustawa o stopniach i tytule naukowym oraz o stopniach i tytule w zakresie sztuki z dnia 14 marca 2003; Dz. U. z 2003 r., nr 65, poz. 595 z późniejszymi zmianami*) and therefore I recommend Mr Stephen Ochieng Kabasa thesis to be accepted by the Scientific Council of the Institute of Chemistry and Nuclear Technology in Warsaw for admittance to further stages of the doctoral degree procedure.

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