REVIEW

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Member of the scientific jury for the competition for the academic position "associate professor" professional direction 4.2 "Chemical Sciences", scientific specialty "Chemical Kinetics and Catalysis", announced in SG no. 47 of 04.06.2024

In the competition announced by the Institute of Catalysis - BAS for the academic position of "associate professor" for the needs of the laboratory "Design and characterization of catalytic materials" in the thematic direction "Application of EPR spectroscopy for the study of radical processes", one candidate participated - chief assistant prof Ralitsa Boykova Mladenova, PhD. All the necessary documents specified in the Regulations for the conditions and procedures for acquiring scientific degrees and for holding academic positions at the Institute of Catalysis (IC) - BAS have been submitted.

Brief biographical details of the applicant

Dr. Ralitsa Mladenova graduated from Sofia University "St. Cl. Ohridski" in 2000. In 2001, he started working at the Institute of Catalysis - BAS as a chemist. In 2007, he received the educational and scientific degree "Philosopher Doctor", defending a dissertation on the topic "EPR STUDY OF THERMALLY GENERATED FREE RADICALS IN FOOD". In 2008, Dr. Mladenova was elected as the II century, and in 2011 - for chief assistant. The professional development and the positions held prove that the candidate, Dr. Mladenova, meets the procedural requirements for holding the academic position " associate professor".

Review of the candidate's research activity

Dr. Ralitsa Mladenova participated in the competition with 22 scientific papers, such as: 20 scientific publications are printed in international refereed publications with an impact factor (5 of them are in Q1, 8 in Q2, 3 in Q3 and 4 in Q4) and 2 publications that are not referenced and indexed in the global referencing and indexing system. Ch. assistant prof R. Mladenova is the first author in five of the publications and is listed as the corresponding author in 6 of them. The total number of noticed citations on the works up to the time of submission is 117, and that on the publications participating in the competition is 64. Based on all published works included in the ISI database, Dr. Mladenova's Hirsch Index (H) is 7 (Scopus).

According to the submitted report on the implementation of the minimum national and additional requirements of the IC for occupying the academic position "associate professor" chief assistant prof

Dr. Ralitsa Mladenova has fulfilled all the requirements, and they have even been significantly increased.

Research projects. For the period 2005-2023 Dr. Mladenova participated in 10 projects, 1 of which she was the head of. The projects are with the "Scientific Research" Fund (5 pieces), with the World Federation of Scientists (1 piece), where he is the head, along the lines of the EDB with the Institute of Catalysis, IBHF RAS, Moscow and the Institute of Chemical Physics, RAS, Moscow, Russia. The candidate's participation in these projects proves that she is a desirable expert in the field of EPR spectroscopy.

- Participation in national and international scientific forums. A total of 27 participations in scientific forums were presented, where the candidate presented poster and oral reports.

Analysis of the main scientific contributions

The habilitation report includes publications B1 - B8, in 5 of which Dr. Mladenova is listed as first author, and in 6 as corresponding author. In the presented scientific works, the aim is to describe the studies on the effect of radiation treatment with gamma radiation on the radical scavenging activity (anti-radical) of some natural products and foods, carried out by the method of electron paramagnetic resonance (EPR) spectroscopy. Some of the articles include additional studies, such as spectrophotometric determination of total phenolic and flavonoid content, as well as high performance liquid chromatography (HPLC) analysis of the samples for a more in-depth explanation of the results obtained on the effect of high energy radiation irradiation on the antiradical activity of the samples. Due to the detailed scientific report on Dr. Mladenova's scientific research and contributions, the main scientific contributions of the research work in the habilitation work can be summarized thematically in the following directions:

Investigation of the effect of gamma irradiation on the radical-trapping activity of bee products [B1, B3, B4, B5] with the EPR method.

– The effect of gamma irradiation on the anti-radical activity of propolis, bee bread and pollen was evaluated, in order to make a correlation with their polyphenolic content, as well as to study the radical processes occurring as a result of the irradiation. In order to achieve the goal, based on the decrease in the intensity of the EPR signal of the stable DPPH radical upon the addition of a certain amount of extracts of non-irradiated and irradiated bee pollen (two harvests), bee bread and propolis, the dependence of trapped DPPH radicals (%) of the extract volume (ml) of the studied samples.

– The relationship between the percentages of trapped DPPH radicals and the amount of non-irradiated and irradiated propolis extracts was studied. The obtained results show that the radical-trapping activity slightly decreases in the samples irradiated with 2 and 10 kGy by approximately 9% and 6%, respectively, while at 5 kGy irradiation has no effect.

– Bee pollen was studied, and it was found that different doses of gamma radiation had different effects on the radical scavenging ability of bee pollen.

- From the results of studies on bee products, it is summarized that the optimal dose for irradiation of bee products for the purpose of microbial decontamination and extension of their shelf life is 5 kGy, and leads to an increase in antioxidant activity in bee bread and bee pollen, while in propolis no effect was found.

Investigation of the effect of gamma radiation treatment on the radical-trapping activity of fruits [B2, B6] by the EPR method.

– A dry rosehip seed residue was studied and the results showed that it possessed radical scavenging properties that increased by approximately 19% after 10 and 25 kGy irradiation. One of the probable reasons for this positive effect is the increase in phenolic content after irradiation, due to decomposition of some high molecular weight polyphenols as a result of interaction with radiation-induced radicals and the formation of more phenolic compounds with smaller structures.

– The dependence between trapped DPPH radicals (in %) and the amount of extracts from unirradiated and irradiated with 0.05, 2 and 10 kGy Goji berries was evaluated. The results reported that the antiradical activity increased with increasing radiation dose.

Investigation of the effect of gamma radiation treatment on the radical scavenging activity of nuts [B7, B8] by the EPR method.

– It was found that the radical scavenging activity of peanuts decreased with increasing irradiation dose. It has been shown that the antiradical activity of the sample irradiated with 25 kGy is time-dependent and further decreases by 16% six months after irradiation, compared to the measurements made several hours after treatment, while in the sample irradiated with 10 kGy it does not change over time.

– The radical scavenging activity of non-irradiated and irradiated peanuts was studied and an increase in the percentage of DPPH radicals scavenged as a function of time was found.

–The same effect of post-irradiation time on antiradical activity as for peanuts was found in hazelnut samples [B8]. The results show that six months after irradiation in the radical scavenging activity of hazelnuts treated with 10 kGy there is no change, while in the samples irradiated with 25 kGy it decreases six months after the radiation treatment.

From the included scientific works in the habilitation report, the following contributions were made:

1) Electron paramagnetic resonance is a suitable technique for evaluating the effect of radiation treatment on the radical scavenging activity of natural products and foods.

2) For the first time, the EPR method was used to study the generation of free radicals as a result of gamma-irradiation, as well as its influence on the anti-radical capacity of the studied samples.
3) All tested samples exhibit anti-radical activity, as their treatment with high-energy radiation for the purpose of disinfection and extension of their shelf life leads to its increase or decrease, depending on the absorbed dose of radiation, the source material and solvent used during extraction, as well as on storage time. In other cases, radiation treatment with some doses of gamma radiation did not cause significant changes in the radical scavenging activity of the samples.
4) The EPR method is effective for determining the optimal dose of high energy radiation for the purpose of microbial decontamination, leading to an increase in antioxidant activity or without detecting a change.

The scientific works presented by Dr. R. Mladenova, outside the list of the habilitation thesis, were made on 14 scientific publications (publications from G1 to G14), where the scientific and scientific-applied contributions are in three main directions:
1) Analysis of the effect of gamma-irradiation on the antiradical properties of foods and organic compounds using the EPR spectroscopy method [D3, D4].
Dr. R. Mladenova works mainly in this direction, which is a continuation of the contribution nature of the works from the Habilitation report. The object of research are studies on the effect of gamma radiation on the antiradical activity of almonds and some organic compounds - ascorbic acid (AA), cysteine (Cys) and diphenylamine (DPA). Due to the detailed report on the contribution nature of the papers (a total of 14 papers), below I will briefly present the main scientific and applied contributions of the candidate.

- Time dependence of 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity of 10 and 25 kGy irradiated and untreated defatted almonds was investigated. A gradual increase in antiradical activity over time was observed.
- Sucrose and ascorbic acid were compared and it was found that the addition of ascorbic acid to sucrose resulted in a decrease in its dosimetric response. This fact is related to the antiradical activity of ascorbic acid.
- An EPR method was evaluated using the stable DPPH radical in order to find the relationship between the antiradical capacity of the substances mixed with sucrose and the reduced EPR response of sucrose irradiated with gamma radiation during simultaneous irradiation.
- The relevant conclusions were drawn from the studies: 1. Substances with antiradical activity added to sucrose (AA, Cys and DPA) reduce the EPR response of sucrose, which means that the new mixed materials do not show better dosimetric properties than pure sucrose; 2.

Radiation treatment of almond leads to a slight decrease in its anti-radical properties, which is more pronounced in the samples irradiated with 10 kGy.

2) *Study of free radicals and the effect of external influences such as high energy radiation, etc. for organic substances [D11, D12, D13, D14] with the EPR spectroscopy method.*

- With the method of electronic paramagnetic resonance, important information was obtained about the type and stability of the generated paramagnetic particles in the studied samples, as a result of external influences, such as irradiation with high energy radiation, heating, etc.
- With the EPR method, the effect of the method of preparation of some foods, such as pasta products, and the storage conditions on the amount of induced radicals in them was established. From the research it can be concluded that vacuum drying protects the pasta from the generation of free radicals. Also, the storage of pasta products in an inert atmosphere protects them from oxidation processes.
- With the methods of electronic paramagnetic resonance and infrared spectroscopy with Fourier transformation, no destruction of the primary structure of hyaluronic acid hydrogel was detected after irradiation with X-rays and various types of laser radiation.
- EPR spectroscopy is a sensitive and efficient analytical technique that has identified radiation treatment in green tea samples.

3) *Characterization of catalytic materials [G1, G2, G5, G6, G7, G8, G9, G10] with EPR spectroscopy.*

- EPR spectroscopy was used to determine the oxidation and coordination state of the paramagnetic ions in the catalytic materials, which is important for explaining their catalytic activity. Information was also obtained on the nature of the defects (surface defects, radicals, free and trapped charge carriers or clusters) and the influence of the doping agent on the structure of the catalytic material as well as on its photocatalytic properties was established.
- Modification of ZnO and TiO_2 with silver ions by photofixation plays a positive role in the photocatalytic process.
- The use of Mentha arvensis leaf plant extract in the synthesis of nanosized ZnO nanoparticles leads to changes in their structure detected by EPR, which are responsible for the increased photocatalytic decolorization rate of the malachite green dye.
- In the case of doping TiO_2 with P_2O_5, more lattice defects are induced, which are one of the reasons for the increase in photocatalytic efficiency compared to the undoped material. It was also found that the photocatalytic ability of the phosphorus-doped TiO_2 samples increased with

decreasing phosphorus dopant content. Titanium photocatalysts containing 1.25 mol% P additive show the highest degree of degradation of the RB5 dye (82%) under UV irradiation.

- EPR studies of ZrO_2 confirm the presence of oxygen vacancies, along with Zr^{3+} ions, the two crystal defects playing a significant role in exhibiting the photoluminescent properties of the material.
- EPR analysis confirms structural modifications and higher catalytic activity in nitrogen-doped ZrO_2 compared to undoped.

Conclusion

The scientific contributions of Ch. assistant professor Ralitsa Boykova Mladenova, PhD are mainly scientifically applied in nature, related to describing the studies on the effect of radiation treatment with gamma radiation on the radical scavenging activity (anti-radical) of some natural products and foods, carried out by the method of electron paramagnetic resonance (EPR) spectroscopy. Dr. Mladenova made an outstanding contribution to the development of EPR spectroscopy in the scientific laboratory "Design and Characterization of Catalytic Materials" at the Institute of Catalysis at the BAS.

The works of Dr. Ralitsa Mladenova are innovative not only in Bulgaria, but also at the world level. In terms of volume and quality, all scientometric indicators of ch. assistant professor Mladenova meets the recommended requirements for holding the academic position "associate professor" according to the Regulations of IC - BAS for the acquisition of scientific degrees and holding academic positions.

On the basis of the above, I am pleased to recommend to the respected members of the Scientific Jury at IC - BAS and to the honorable Scientific Council of IC - BAS to award the chief assistant prof. Dr. Ralitsa Boykova Mladenova the academic position of "ASSOCIATE PROFESSOR" in the scientific specialty "Chemical Kinetics and catalysis", under the thematic direction "EPR spectroscopy and quality of life" for the needs of IC - BAS.

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(assoc prof G. Nikolova, PhD)