REFEREE REPORT

by Plamen Kirilov Stefanov, Prof., PhD,
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regarding a competition for the occupation of the academic position "Professor", for the needs of Laboratory "Chemistry of solid fuels" at the Institute of Organic Chemistry with the Center of Phytochemistry - BAS (IOCCP), professional direction 4.2. Chemical Sciences, specialty 01.05.10 "Organic Chemistry"

In the competition for the academic position "Professor", announced in the "State Gazette", issue. 40/31.05.2022 and on the website of IOCCP-BAS, the only candidate Assoc. Prof. PhD Boyko GeorgievTsyntsarski from the Institute of Organic Chemistry with Centre of Phytochemistry has submitted the respective documents.

1. General presentation of the received materials

The materials, presented for reviewing, completely correspond to the requirements of the Law for Scientific Development in Bulgaria, the Rules of its Application as well as to the Internal Rules and Regulations of the Institute Organic Chemistry with Center for Phytochemistry (IOCCP) for acquiring the academic position "Professor".

Assoc. Prof. Tsyntsarski has published a total of 106 scientific works, and for participation in the present competition he submitted 17 scientific publications, which do not repeat those presented in other competitions for holding academic positions and acquiring scientific degrees. All of them fall within the field of the competition and are therefore subject to review. To participate in the competition, Assoc. Prof. Tsintsarski has submitted the necessary documents: CV, copy of diploma for awarded PhD degree, diploma for Associate Professor; extended habilitation reference in Bulgarian and English, general list of publications, general list of citations, list of publications for participation in the competition, list of participation in scientific forums after habilitation, certificate of fulfillment of the minimum and additional requirements of BAS and IOCCP-BAS. The documents contain the full texts of publications and evidences of participation in scientific forums and research projects.

2. Brief biographical data about the candidate

Boyko Tsintsarski completed his secondary education at the National-Natural Mathematical High School «Acad. L. Chakalov», chemistry class in 1990. He graduated in 1996 with a Master's degree in "Inorganic and Analytical Chemistry" from the Faculty of Chemistry at Sofia University "St. Kliment Ohridski", thesis topic: "Synthesis of Rb-doped YBaCuO films". In 2004 he defended his doctoral thesis on the topic "Selective catalytic reduction of hydrocarbons on Co−ZSM-5 IR spectroscopic study of the mechanism of the process" in IGIC-BAS. Assoc. Prof. Tsintsarski's scientific career developed mainly at IOCCP-BAS, where he held the following academic positions: chemist (2003-2006); assistant (2006-2008); Assistant Professor (2008-2013) and Associate Professor (2013-present). He completed a short-term specialization in 2014 at the Center for Polymer and Carbon Materials, Polish Academy of Sciences, Zabrze, Poland. He is currently the Head of the "Chemistry of Solid Fuels" laboratory at IOCCP-BAS.

3. General characteristics of the applicant's activities Evaluation of the applicant's scientific and applied scientific activity

Assoc.Prof. Tsintsarski 's scientometric data includes a total of 106 scientific publications, of which 89 are in journals with IF, 13 in journals with SJR, 3 in non-refereed scientific journals without IF, a book chapter indexed in Scopus. The publications with which he participated in the competition for the academic position of "professor" numbered 17, all published after 2012 and distributed in journals by quartiles as follows: Q1-8; Q2-8 and Q4-1 articles. For me, the relatively small number of publications submitted for the competition arouses some confusion, since in the competition for docent the candidate participated with 29 articles, half of which are in Q1. Among the submissions for the present competition are articles in the authoritative Microporous and Mesoporous Materials JCR-IF (Web of Science):4.182, Journal of Hydrogen Energy JCR-IF (Web of Science):4.229, Carbon JCR-IF (Web of Science):9.594 and etc.

The number of observed citations on all publications of the applicant is 1096. The Hirsch index (Scopus) calculated on this basis is 17. The applicant did not give the number of observed citations only on publications included in the contest, which would be an indication of the actuality and relevance of his research. In my estimation, from the presented list of citations, the number of these citations is 112, which is relatively small in number, but this may also be due to the fact that 7 of the publications are after year 2020.

The results of Assoc.Prof. Tsintsarski's scientific research have been presented at 12 international and national scientific forums, through 11 scientific reports and 1 poster report. The two plenary reports presented by him at international forums are a recognition of the importance of his scientific research. The candidate has submitted documents for participation in 8 projects, of which 3 are under the National Program "Young Scientists and Postdoctoral Fellows", one with international funding under the "European Training Networks" program and one project financed by the "Scientific Research" fund. Assoc. Prof. Tsintsarski has been the head of one project financed by the "Scientific Research" fund and two equivalent change projects with scientists from Romania and Poland. His participation as the leader of these projects is a proof of Assoc.Prof. Tsintsarski 's ability to organize and lead scientific research.

The presented report on the minimum requirements to the scientific activity of the candidates for the academic position " Professor" shows that for all groups of indicators, published in the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Regulations for its implementation, as well as the additional criteria of BAS and IOCCP, performed points by Assoc.Prof. Tsintsarski exceeded the required ones, namely according to indicator B (habilitation work) the required minimum is 100, while the fulfilled were 102, and in group D (scientific publications in publications referred in WoS or Scopus) with the required 250 points were fulfilled 270. In group D, which refers to citations of scientific publications referenced and indexed in WoS or Scopus databases, with a requirement of 200 items, 1,634 items were presented. I think that the points on this indicator are controversial because, in my opinion, the requirement for citations applies only to works submitted for participation in the competition and not to citations of all publications after habilitation. Accordingly, the number of citations is 112, and then the points are 224. For indicator E, referring to participation in a national scientific or educational project: the requirement is 150 points, and 192 points are declared.

The detailed review of the results summarized by the candidate, reflected in the Extended Habilitation report, outlines the main focus of his research activity on the development of innovative methods for the utilization of organic raw materials and organic

waste from various productions. The application of these methods allows obtaining efficient nanoporous carbon adsorbents, composites and liquid and gas energy sources.
The conducted research and the published results have marked scientific and scientific-applied contributions in the relevant fields of science. The contributions can be formulated as a rationale for a new eco-friendly approach; creation of new synthesis methods; obtaining new facts.
According to the presented habilitation reference, Assoc. Prof. Tsintsarski's scientific contributions are the result of interdisciplinary research and can be considered in the following main directions:
I. Development of methods for obtaining new carbon materials based on various organic raw materials. Preparation of carbon materials by thermochemical treatment, pyrolysis, carbonization, activation. Detailed characterization of precursors and final carbon products

The investigations related to the first direction occupy the most essential part of the scientific work of Assoc. Prof.Tsintsarski and are summarized in 5 main publications of the habilitation thesis. The object of research are the processes taking place during the thermochemical treatment of mixtures of organic compounds and determining the conditions for the formation of a carbon material with a developed porous structure and a high specific surface area.
The development of an innovative method for preparation, based on various precursors (waste biomass, polymers, coal, etc.), carbon materials with a high specific surface area and micro-/meso-porous texture can be assessed as a significant contribution.
The physicochemical characteristics and chemical character of the surface of the obtained carbon materials, which play an essential role in their various applications, have been studied. The influence of the conditions of the thermochemical treatment on the content of various oxygen-containing functional groups with a slightly acidic and basic character on the surface of the final products was determined. The nature of carbon atoms located at the edge of graphene layers as highly reactive centers that determine the surface reactivity, surface and catalytic reactions of the corresponding carbon material has been clarified [B3].
Carbon adsorbents with a developed porous structure and with an alkaline character on the surface were obtained for the first time by high-temperature hydro-pyrolysis of natural asphaltites. The obtained carbon adsorbents show good adsorption properties, despite the high content of ash and sulfur [B2]. Activated carbons with different textural and chemical surface characteristics (specific surface area 600-900 m2 /g) and with possible application as a carrier for cobalt catalysts have been synthesized from waste biomass and low-rank coal [B3].
In practical relation, these studies contribute to the development of an innovative method for the efficient utilization of algae waste in the production of biodiesel. The optimal conditions were found for the treatment of the raw material (waste from algae), allowing the production of valuable gas and liquid products, as well as high-quality activated carbon [B2].

II. Study of the influence of various factors on the processes of synthesis of carbon materials.

The relationship of the chemical composition and texture of the raw materials with the difference in the nature of the chemical transformations and changes in their structure as a result of the thermochemical treatment is clarified. As a result, the dependences between the chemical composition and the texture of the raw material and the properties of the final product were determined.
As a practical contribution in this aspect is the preparation of a carbon adsorbent with a developed pore structure from Sirnak asphaltites by a suitable two-step process/carbonization and subsequent activation [B3].

III. Application for nanoporous carbon materials as catalysts, adsorbents for water and air purification, composites for hydrogen production and storage, etc. Environmental problems.

A significant part of the research in this direction is aimed at developing adsorbents and catalysts for the elimination of organic pollutants from water and air and innovative metal-carbon nanocomposites for hydrogen storage.

As a contribution to the fight against the effects of global warming, research on activated carbon synthesized from organic materials for the capture of CO_2 is of significant interest. An essential requirement for these materials is the presence of a high specific surface area, adjustable porosity and chemical surface properties.

For this purpose, three different types of activated carbon have been synthesized by a combination of pyrolysis and steam activation from agricultural raw materials - pits of peaches, olives and apricots. [G4,G10].

Nanoporous carbon obtained from apricot pits was found to have the highest volume of micropores (predominantly ultramicropores), while carbon from olive pits had the highest percentage of meso- and macropores. A study of their chemical composition shows that the synthesized activated carbons have an alkaline character on the surface, with the presence of both weakly acidic and basic surface functional groups. A comparison of their activity against CO_2 shows that the nanoporous apricot stone carbon has the highest adsorption capacity.

Another direction in Assoc.Prof. Tsintsarski's research is the development of new materials for hydrogen storage. The innovative idea is to obtain cheap metal-carbon composites based on various carbon materials (nanoporous carbon, carbon foam, graphene, etc. from waste products from industry and transport - polymers, oils, waste from the wood processing, canning industry, etc.), and the storage of hydrogen is in the form of metal hydrides or in the form of methanol [G1, G8, G10]. The sorption of hydrogen on different composites - 95 wt% Mg-5 wt% C, 80 wt % MgH_2-15 wt % Ni-5 wt % activated carbon, 90 wt%MgH_2-5 wt%Ni-5 wt%POW was investigated. Different types of activated carbon were used as a carrier - obtained from apricot pits, from bean pods and polyolefin wax. Apricot stone activated carbon was found to have a more pronounced positive effect on the hydrogen sorption performance of magnesium than bean pod carbon, possibly due to better protection of the Mg surface from oxidation and particle agglomeration during cycling of hydrogenation/dehydrogenation. Activated carbon derived from polymers positively affects the hydrogen absorption/desorption kinetics of magnesium, leading to an increased rate of the hydration reaction and a high absorption capacity in long-term cycling.

An intelligent integrated scheme has been developed for the full utilization of biomass for clean energy production. The proposed approach includes production of activated carbon-based catalysts for methanol decomposition as source of hydrogen. In this scheme, carbons with different texture and surface functionality were used as carriers of the active phase of iron, zinc and ferrite catalysts. It was established that the dispersion and composition of the deposited active phase can be controlled by the type of carbon precursor used and by its different activation and processing, which in turn determines the catalytic activity [G2, G3, G7].

Another, particularly important from an ecological point of view, direction in the candidate's research activity is the development of effective adsorbents for the extraction of toxic pollutants from wastewater by thermochemical treatment of organic waste. This approach is very effective because it helps to utilize waste from agricultural and industrial production, which is processed

into highly efficient carbon adsorbents to solve environmental problems. Original scientific contributions can be noted in several studies as follows.
From polymer waste - a mixture of polyolefin wax and phenol formaldehyde resin - activated carbon with high adsorption activity against phenolic derivatives - pentachlorophenol, m-aminophenol and p-nitrophenol - was synthesized. It was found that the adsorption capacity of activated carbon towards these phenolic compounds depends on the porosity parameters and on the surface chemistry (basic/acidic nature of the surface functionalities) [D11].
A new type of hybrid material suitable for the removal of metal cations from wastewater was obtained by combining two components - a polymer membrane and 4% or 8%. powdered activated carbon, thus combining the ultrafiltration characteristics of polymer membranes with the adsorption properties of carbon. It was found that the hybrid organic-inorganic membranes show a high adsorption capacity (51%) towards Ni^{2+} cations in aqueous solutions [D12].
Activated carbon obtained from a polymer waste product showed a high adsorption capacity for mercury ions (196 mg/g), with the removal of Hg^{2+} from aqueous solutions increasing with increasing pH from 2 to 5, and slightly decreasing at pH > 6 [B4].

In the last part of the habilitation report, the candidate's vision for future research on the subject of the competition is presented. It is planned to continue and deepen the research on carbon-containing materials and their application, which is in line with modern trends in chemical materials science. The plans include the synthesis of new efficient carbon materials – C/C composites, carbon foam, carbon nanotubes, graphene; development of new methods for the synthesis of carbon adsorbents with suitable pore size, search for suitable modification methods. Research will be conducted in current areas of application of carbon materials - hydrogen storage, battery electrodes, adsorbents for various bacteria and viruses.

4. Assessment of the candidate's personal contribution

The most part of the research presented in the publications for the competition has an interdisciplinary nature with a large number of participants. This makes it difficult to determine the candidate's personal contribution. However, from the presented general list of the candidate's publications, it can be seen that he has been working in this field for many years and a significant part of his work is devoted to the preparation, characterization and application of carbon materials, and he obtained his habilitation on the basis of this subject. This suggests that Assoc.Prof. Tsintsarski undoubtedly has scientific competence regarding synthesis methods, for studying their properties and finding actual areas of application of the developed carbon materials. In the works presented as the equivalent of the Habilitation work - B1-B5, the candidate is the leading author, which is indicative of his leading role in the research done and the generalization of the obtained results. His qualities as a leading researcher in the field of the current competition can also be judged by his election as the Head of the Laboratory "Chemistry of Solid Fuels" at IOCCP-BAS.

5. Critical remarks and recommendations

I have critical remarks regarding the submitted materials for the competition. For the most part, the lists of articles and citations are not presented in a proper, orderly manner, which makes their analysis difficult. A particularly bad impression is made by the extended habilitation reference, in which lacks a more comprehensive summary of the applicant's contributions. Instead, it includes translated abstracts of the most publications, greatly increasing its volume. The applicant gives a lot of redundant details by listing the research methods, including detailed

data on the characteristics of the materials, etc. The text contains a large number of technical errors, such as omitted letters, repetition of words and even confusing phrases, which is not up to the level of a competition for a professor. The extended habilitation report surprisingly extensively comments on contributions from the work labeled X7 (Separation and Purification Technology, 116, 2013, 214), but it is not included in the list of publications for participation in the competition and has no imprint attached.

These critical remarks refer entirely to the gaps in the submitted materials for the competition, but do not detract from the quality of the applicant's scientific achievements and contributions, so that a positive impression of their high scientific level remains.

My recommendation to the candidate is that in the future, when participating in prestigious competitions, he should be more responsible and thorough in the preparation of the sets of materials.

CONCLUSION

Based on the materials submitted for the competition by Associate Professor Boyko Georgiev Cintsarski, I believe that his candidacy fully meets the criteria for occupying the academic position "Professor", defined by the Law on the Development of the Academic Staff in the Republic of Bulgaria, the Rules for its Implementation, the Regulations for the terms and conditions for occupying academic positions at BAS, as well as the Regulations for the terms and conditions for acquiring scientific degrees and for occupying academic positions at IOCCP-BAS. The candidate is an established scientist, with a clearly defined scientific profile and proven scientific and scientific-applied contributions. The direction in which he works is current and of a large scientific and applied perspective. On the basis of the above, I recommend the members of the Scientific Jury to support the election of Assoc. Prof. Dr. Boyko Georgiev Cintsarski for the academic position of "Professor" in professional direction 4.2."Chemical Sciences", scientific specialty "Organic Chemistry".

30.09.2022 Reviewer:

/prof. Dr. Plamen Stefanov/