Candidate: Alcina Johnson Sudagar
Thesis title: 'Synthesis, characterization, and testing of catalytic nanomaterials – greener route to synthetic methods'

Reviewer's Report

This dissertation has been developed within the wider context of 'green chemistry', focusing on the exploration and development of new nanomaterials, specifically for the purpose of obtaining new 'green' catalysts to be deployed in synthetic methodologies.

The area is certainly a very topical one, of great interests to both materials scientists and organic chemists alike, as the scientific community embraces the new challenges posed by the current environmental crisis, working towards important goals that will benefit society and our planet.

The work carried out by the candidate has focused on two main approaches to achieve the same objective: on one hand the use of the molecular imprinting approach to obtained films to be used for the selective electrosynthesis of an industrially important chemical, on the other hand, instead, the preparation of silver-based nanocomposites, obtained from greener sources. The thesis is well organised in five chapters, the first one is the introduction to the research area, followed by a second chapter on the materials and methods used together with a very useful description of the techniques used during the project; the results and discussion part is developed in two chapters, one focusing on the work with the imprinted polymers, and the second one on the silver nanocomposite. The final chapter presents the conclusions, an overall view of the work and some discussions on future perspectives. The dissertation is well written and very well presented, with clear colour figures and captions that facilitate the understanding of the experimental work carried out. This body of work represents a clear scientific advance in the field of greener catalysis, as evidenced by the scientific accomplishments of the candidate, with two papers already published from the work related to silver nanocomposites and two papers in preparation, one of which focusing on the molecular imprinting work, as well the active participation to three conferences.

The introduction is extensive and covers in depth the topics of the work, starting with a clear explanation of the concept of selectivity, which is fundamental in this work, followed by a clear description of catalysis and its importance within chemistry and more specifically

organic chemistry. There is then an extensive section on molecular imprinted polymers, covering both the principles and a general overview of the different synthetic methodologies, with a more detailed description of electropolymerisation. The latter is particularly important for the reader, as it sets the background against which the work has developed in Chapter 3. There is an impressive coverage of the literature with multiple papers cited for each different types of monomers/polymers developed via the electropolymerisation approach. In the second part of the introduction the candidate has provided an introduction to green nanomaterials for catalysis, with overview of the synthetic approaches and trying to focus more specifically on the 'green' approaches, followed by a very detailed overview of the advantages of developing silver-containing nanomaterials. This part of the introduction is very clear and, importantly, provides all the necessary information to understand why the candidate decide to choose this type of metal-containing nanomaterials for her work. Once again the coverage of the literature is extensive and comprehensive.

Chapter 2 of the dissertation described the experimental work but also includes a very useful section with the theory of the techniques used, which ensures that readers perhaps lacking specific knowledge are able to fully understand the reasons for using such techniques. The explanations of the theory behind the techniques is very clear and the candidate has chosen to present just sufficient details that allow the reader to grasps the basics without getting lost in unnecessary explanations.

Chapter 3 is focused on presenting the results related to the synthesis and characterisation of MIPs prepared electrochemically, using conducting organic polymers. The candidate decided to focus specifically on the electro-oxidation of 2,4-dimethylphenol to afford the product TMBh (3,3',5,5'-tetramethyl-2,2'-biphenol), as a choice of model reaction. 2,2' biphenols are a class of natural products that can be found widely in natural products, and in fact these molecules can form the backbone of larger molecules with important applications both as catalysts but also as active pharmaceutical ingredients. Therefore their synthesis is of great significance for the chemical industry in general, which highlights the importance of having chosen this reaction. There are currently two major challenges related to the industrial synthesis of these molecules: on one side there is the lack of selectivity of the reactions, leading to a variety of side products, often without a real application, while on the other side there are the low chemical yields.

The candidate has carried out an extensive body of work on this challenging objective, with a number of results, especially at the beginning, which provided disappointing results. The initial choice of functional monomer did not lead to satisfying results and therefore the second functional monomer had to be utilised. This led to additional work that afforded some interesting data. The films obtained have been fully characterised and the discussion of the experimental data shows a strong degree of critical thinking and more importantly the results presented fully support the conclusions by the candidate. Of particular note is the work done on the impact that the 'ageing' had on the prepolymerisation mixtures . This is really an interesting part of the work, where multiple techniques, such as UV-Vis, NMR, DLS and AFM were used to provide very good data. On this particular item it would be interesting to have a bit more information on the literature behind this particular topic and whether the conclusions achieved by the candidate, that there is a clear difference between aged solutions and fresh solutions and that the smoothness of the surface is impacted, with less aggregates formed in the ageing solution, is in fact consistent with other literature data. One additional point that is not addressed in the chapter 3 is the choice of using the target molecule as the template for the preparation of imprinted polymers. This is something that is not often done when developing imprinted polymers with catalytic activity, because of the potential risks that the 'catalytic sites' become blocked by the binding with the template during the imprint stage.

The characterisation of the films obtained is very thorough and detailed. There is also a good amount of work on the optimisation of the initial formulations, to study the effect of changes in the formulations, evaluation of film thickness and characteristics. The results are very strong and fully supported by the data presented in the thesis. The increase in selectivity is excellent, obtained by carrying out the electrosynthesis at higher temperature, or in the presence of a variety of additives.

Chapter 4 of the thesis presents the work done in relation to the development of silver-containing nanomaterials, based on the recycling of the large quantities of waste that is produced by the beer industry. The research focused on the analysis of the brewery waste to gain detailed information about its composition and the presence of compounds of interest. Following the synthesis of the nanocomposites, their structure composition and morphology was also studied in details, together with evaluation of the thermal stability . In the last section the preliminary data on the catalytic activity are presented.

The most significant achievement in this part is the development of the 'one pot' synthesis process, that is certainly eco-friendly and that, if adopted, could be run more cheaply, with considerable savings. The preliminary data on the use of these nanocomposites for photo- and electrocatalytic applications are very interesting, although the work will need to be further optimised, due to the issues associated with charge recombination and hindered charge transport.

This dissertation represents an excellent body of work, in a very novel and challenging area of research. The results represent a significant advancement in the body of knowledge currently available and will be of great use to colleague scientists working in the field. The results presented are fully supported by the experimental data included in the thesis and as such this doctoral dissertation meets the conditions specified in Article 187 of the Act of July 20, 2018 Law on Higher Education and Science and the candidate should therefore proceed to the next stage of the examination.

In view of the extensive body of work presented, the details and the explanations of the scientific results, even when these were not as successful as expected, the quality of the writing and evidence of very strong critical and analytical skills, I believe that this dissertation deserve a distinction.

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