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FACULTY OF CHEMICAL TECHNOLOGY AND ENGINEERING
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REFEREE REPORT
of the dissertation entitled "Graphene based materials and their potential applications"

A PhD thesis submitted by Mr. Dawid Pakulski provides as a scientific achievement to award the doctoral degree. The dissertation has been supervised by Prof. Violetta Patroniak (AMU), dr. Artur Ciesielski (HDR) (Unistra) and co-supervised by Prof. Paolo Samori (Unistra). The research described in the Thesis was realized within the double doctorate program funded by French Embassy in Poland. The topic is focused on the multidisciplinary field of synthesis and functionalization of graphene and graphene oxide for adsorption and energy storage performance. The thesis contains 159 pages divided into following main sections:

- Summary in three languages (Polish, English and French),
- Introduction – 42 pages,
- Characterization Techniques – 22 pages,
- three Experimental chapters – 53 pages,
- Conclusions.

Additionally, the thesis contains list of abbreviations, Statement ofwork, publications list and achievements. The structure is logical and clear and slightly different from typical PhD thesis. Especially, the distribution of the references after each section is surprising but very helpful. The thesis is carefully written. Some editing mistakes have been noticed.

The review will consist of few aspects which will highlight the quality of science and some questions/comments described in the thesis.

The **Introduction** section is well written and contains the most important aspects on 2D materials and their sensing performances of metal ions, (bio)molecules such as bimolecular fluorescence sensors, field-effect transistors for biomolecular sensors, electrochemical biomolecular sensors, biomolecular sensing via surface enhanced raman scattering.

Experimental section briefly describes all the techniques employed in the materials characterization. Here I have one remark: in order to study flake-like material atomic force microscopy is typically employed - this technique is missing in the samples characterization. Why? It would be of great interest to couple AFM analysis with all other presented techniques.

In Chapter 3 Mr. Dawid Pakulski describes adsorption properties on graphene oxide-branched polyethyleneimine (BPEI-GO composite) materials. The synthetic route appeared to be easy and obtained 3D composite exhibited promising adsorption affinity, stability and reusability in the process of heavy metal ions adsorption (10 cycles). Obtained GO based 3D foams have been tested in the adsorption of ions of lead, copper and cadmium. Its efficiency is attributed mainly to the presence of oxygen- and nitrogen-containing functional groups, interacting at the supramolecular level (via supramolecular pockets) with the metal ions. As an effect the composite served much better as heavy metals ions adsorbent than other materials based on GO reported in state of the art. Reusability was also very efficient due to non-covalent interaction between GO and metal ions allowing easy regeneration. The adsorption isotherms were best fitted to Langmuir model indicating that the adsorption process is not monolayer coverage related. Thermodynamic data provided information that the adsorption process of heavy metal ions had exothermic and spontaneous nature. However there are some comments/questions to this part of the thesis:

Usually, three kinetic models: the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic model, are used to elucidate the rate of adsorption. Why not all of them are used in the work? What could we learn from missing model?

Next chapter (Chapter 4) is also focused on design of 3D composites based on GO. Here, novel mesoporous silica - graphene oxide hybrid material (SiO_2NH_2-GO) serving as highly efficient and fast adsorbent for removal of cationic organic dyes such as methylene blue (MB), rhodamine B (RhB)

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and methyl violet (MV), from water has been investigated. The sample is well characterized, however TEM analysis would be very interesting to reveal morphology in greater details.

Additionally, another question could be here addressed:

Starting material in Chapter 3 surface area was ~10 g/m^2 and in Chapter 4 it was ~100 g/m^2. Why could it happen?

The results on adsorption experiments clearly indicate that all investigated dyes (MB, RhB and MV) can be efficiently adsorbed at pH10 with very high maximum adsorption capacity of 300, 358 and 178 mg g-1 , correspondingly. However, what is more important the system shows excellent adsorption efficiency of ~99.7% for MB, RhB and MV in 3 min, which is extremely fast in respect to the state of the art. Along with stability and reusability this adsorbant is highly-efficient and low-cost candidate as water purification technologies.

3D composite based on graphene was a presented in Chapter 5. Here, Mr Pakulski proposed a strategy to produce a novel molecular hybrid based on Keplerate type polyoxometalates POM (Mo132) functionalized with dodecyltrimethylammonium bromide (DTAB) and Graphene. Graphene was electrochemically exfoliated from graphite. The procedure resulted in the formation of porous 3D structures investigated as active material in supercapacitors. The sample was characterized with suitable techniques, however, atomic force microscopy as a powerful tool to reveal the flake size/thickness is also missing. In the section on the electrochemical performance as supercapacitor Mr Pakulski presented data of specific capacitance from CV curves, and cycling stability of the supercapacitor composed of the samples as active electrode material. This is not enough to provide full electrochemical analysis of the potential material. What kind of electrochemical measurements are missing?

In summary, PhD thesis contains original and valuable scientific results on the synthesis and application of 3D porous based on graphene or graphene oxide. The respective materials have been investigated in adsorption of heave metals ions and energy storage device. I have to admit that this is valuable contribution to chemistry and nanotechnology fields. Therefore, this is interesting multidisciplinary thesis. Some of the data were published in very good journals with high impact factors what also indicate their originality and high quality. It also proves that the conducted research lies in the most current research field – graphene based composites. Constructing 3D materials out of

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2D graphene seems to be extremely promising strategy to find its real application. The thesis is well written and the figures are also very clear and consequently presented. Therefore, I deeply believe that the dissertation certainly meets the requirements of the doctorate degree specified by the Ministry of Science and Higher Education (Act on Academic Degrees and Academic Title) and therefore, I recommend the Faculty of Chemistry at Adam Mickiewicz University in Poznań awarding the Candidate the degree of Doctor.

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