Review

of dissertation thesis

"Selected Sorption Properties of Nanofibers Assembly"

by

Yan Wang, M. Eng.

The thesis consists of 119 pages including literature references and lists of symbols, figures and tables. It is structured into 5 chapters.

Chapter 1 (Introduction) gives a brief background on Polyamide 6 fibers. The most important part of the chapter is the formulation and description of the aim of the work, where the reasons for this study are explained. In this section, I would appreciate a little more structured description of main goals of the thesis.

Chapter 2 (Literature Review) is focused on all important aspects necessary to understand material properties of Polyamide 6, adsorption mechanisms and their models, and nanotechnology/nanomaterials related to the research activities of the author (electrospinning, nanoparticles, surface modifications).
Significant portion of the text is dedicated to photocatalytic properties of TiO_2 particles bonded on the nanofiber surface, as an introduction to corresponding research activities of the author described in following chapters. This topic exceeds the (probably) original scope of the thesis, as these processes are only weakly related to adsorption. However, the application field (removing non-desired substances from fluids) is relevant to the title of the thesis.
The chapter is written with adequate care, and it gives sufficient introductory information above the current state of the research field where the thesis indents to contribute.

Chapter 3 (Materials and Methods) is dedicated to the choice and description of both commercial and self-built equipment used in the experimental part of the work, which is the core of the thesis. In this effort, the author is very systematic, descriptions are given in sufficient details. Also, the materials used for the sorption studies are characterized properly. In the chapter, some experimental results are also given, e.g. BET values measured on nanofiber membranes. As these experiments do not deal directly with the sorption study itself, presentation of the results in this part of the thesis is appropriate.

Chapter 4 (Results and Discussion) presents experimental results structured into three parts: (1) dye sorption onto Polyamide 6 nanofiber membrane, (2) dynamic sorption, and (3) surface modifications of the membranes. Nanophotocatalysis has been studied as a self-cleaning mechanism tor the membranes. Again, I have to note that this part of the work is not 100% compatible with the main topic of the thesis (sorption properties); however, its outputs are interesting and relevant to the aim of the study (removal of dye, hormones, etc. from fluids). I value author's effort to correlate experimental data with the theoretical models (Freundlich isotherm – p. 66, Langmuir isotherm – p. 67). Correlation coefficients obtained from the analysis (0.81 and 0.85, respectively) are sufficiently high to prove that the models are good enough for qualitative understanding of the sorption processes at nanofiber membranes. Author's approach to the experiments is systematic. The results are presented clearly, with appropriate comments. The methods and equipment author used are appropriate. Graphs and tables are easy to understand and follow.

In Chapter 5, author clearly summarizes and generalizes the extensive results discussed in details in previous chapter. The conclusions are formulated logically. The results are qualitatively summarized, which corresponds to mostly empirical character of the work. I would appreciate in this part some vision from the author towards practical industrial applicability of the results. Also, I miss some recommendations for continuation of the research in the field.

Concluding notes and recommendations:

1. Author collected extensive and very useful amount of systematic experimental data related to the sorption processes on PA6 nanofiber membranes.
2. Graphical appearance and language of the work is very good.
3. The study is of mostly experimental character. However, author has shown good understanding of the effects observed and fitted obtained data with known theoretical models.
4. Can author comment/explain, why Langmuir isotherm fits better than Freundlich?
5. The BET values obtained for the 2 nanofiber PA6 membranes indicate, that the surface area of the samples corresponds very well to geometrical surface of the fibers (square of fiber diameter ratio is approx. 2.7, BET ratio is approx. 2.6, according to Table 3-1 on page 44). Is there any indication that some "fine" surface structure of the fibers (e.g. "nano-roughness") influences sorption mechanisms of the membrane? How important is BET value for eventual prediction of sorption kinetics and capacity of the material?
6. Author has published 4 journal papers, 16 publications at well attended international conferences, and one book chapter. I consider his publication activities so far to be sufficient prove of his independent scientific ability.
7. The importance of the work for the nanofiber industry is high, as it helps to understand added value of nanofiber materials in many practical applications. The thesis solved just a part of what the industry would need; however, this is a good start and inspiration for eventual continuation of the research in this direction.

I recommend the thesis for the defense
by the Committee for Doctoral Dissertations
of the Faculty of Textile Engineering of the Technical University of Liberec.

Liberec, December 16, 2016

doc. Ing. Stanislav Petrík, CSc.

Opponent's review

This opponent's review was elaborated based on Ing. Jana Drašarová, PhD. (dean of Faculty of Textile, Technical University in Liberec) assignment for review Ph.D. dissertation thesis (ref. no. TUL-16/4814/041920, dated 10. 11. 2016) of **Yan Wang, M.Eng.** entitled **"Selected Sorption Properties of Nanofibers Assembly"**. Tutor of the PhD. student was Prof. Ing. Jakub Wiener, Ph.D.

Theses presented has a technological impact for dyes recovery from the solutions and waste waters.

Polyamide fibers have found a broad application in textile industry due to their properties, such as high mechanical strength, flexibility, abrasion resistance, excellent dyeability, and easy material maintenance. As a sorption material for waste water treatment a polyamide 6 with nanofibrous membrane (PNM) with the ability of removal of bacteria, dye adsorption and hormone removal from the solutions. This capability was improved by the surface treatment of PMN by means of UV light irradiation and water steam, by means of the deposition of TiO_2 nanoparticles. Material characterization as the adsorption substrate was studied by means of adsorption isotherm determination BET (pore size and specific surface area determination), Freundlich and Langmuir isotherms determination for a given pair of adsorption material and adsorbing substrate. Furthermore, there were applied methods of FTIR and UV VIS for characterization of dyes and DSC for the characterization of the physico-chemical properties of the materials under study. Microscopic picture of the PNM was obtained by means of scanning electron microscopy, SEM. Adsorption capacity of the tested materials was performed at various temperatures, pH and dyes concentration on apparatuses constructed at constant flow rate, dynamic sorption process with UV light etc. The chosen methods fully characterize adsorption profile of the tested material PNM for given application.

Major results of the thesis are focused on utilization of PNM as a sorption material. The best for describing the adsorption process, according to the applicant's judgement seems to be the Langmuir adsorption isotherm, characterizing mainly the monomolecular adsorption. According to the thermodynamic calculations the studied adsorption process is entropy driven spontaneous process in the temperature range of 30 to 50°C, where the concentration and temperature increase consumption of the acidic dye. For different adsorbates studied this effect was negative. Surface treatment of the material further more increases its sorption capacity. For the calculation of the adsorption formal kinetics, the Elovich formula and the pseudo second order kinetics approach were applied. By the latter method and application of the least square calculation there was selected the better fitting model of the given type adsorbent-adsorbate. From the formal point of view, results of the theses and the thesis itself are well written, results are presented in the form of tables and graphs. Thesis represent typical material science oriented study focused on polymeric fibers characterization for textile industry.

Thesis are written in English language in the form of the monograph. Thesis total references cited was 142. There were cited fundamental research articles as well as the latest publications. However the format of the reference list is not fulfilling requirements of the citation standard CSN ISO 690.

Results of the thesis of the applicant Wang were published in 2 scientific papers in impacted journals and two more papers are under evaluation and submitted to the journals. She was attending several scientific conferences at home as well as abroad, she is the coauthor of one contribution in the book entitled "The production, Characterization and Applications of Nanoparticles in Textile Industry" published in 2014.

Questions to be answered during thesis defense:

1) Quantify the reproducibility of your sorption experiments.
2) Verify the results by means of statistical ANOVA analysis.
3) Did you performed desorption experiments as well?

Based on the latter mentioned facts and by the course of law (Higher Education Law No. 111/1998. Sb.) §47 I recommend to accept the PhD. dissertation thesis of Yan Wang, M.Eng. for defense.

In Zlín, December 2, 2016

Doc. Mgr. Barbora Lapčíková, Ph.D.

Associated professor for materials science and engineering
Tomas Bata University in Zlín