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Review Report on the doctoral thesis of Iwona Lupul entitled "Removal of selected toxic compounds from water by adsorption on activated carbon from agricultural by-products"

The concept of the PhD thesis of Iwona Lupul is very interesting. The first addressed issue is comprised by the use of agricultural waste as precursors in the process of their conversion into low-cost adsorbents. The second one is the assessment of the suitability of obtained carbon adsorbents for the removal of pesticides, dyes, heavy metal ions present in groundwater or drinking water. Two precursors for preparation of activated carbons were selected for this study: hemp stem and palm kernel shell. Typical water contaminants (pesticide, dyes and heavy metal ions) were used as adsorbates.

The thesis covers 150 pages altogether, and is enriched by a number of figures (71), equations and chemical reactions (28), and tables (38). The theoretical principles as well as the research part were validated with 235 valuable references.

The PhD thesis begins with an introduction to the subject-matter (chapter I). The main part of the dissertation consists of five chapters (II-VI).

Chapter II presents literature review and has a logical partition. Subchapters 2.1 and 2.2 include the fundamentals of adsorption and mechanism of adsorption from liquid phase. The next subchapters (2.3, 2.4 and 2.5) are devoted to activated carbon and its characteristics, preparation of activated carbons (precursors, physical and chemical activation) and modification of the surface chemistry of activated carbon, respectively.

Subchapter 2.6 is dedicated to a detailed description of the adsorption from aqueous solution: factors affecting the adsorption process, adsorption kinetics and equilibrium.

In the last two subchapters, adsorption of organic compounds (pesticides and dyes) (2.7) and heavy metals (2.8) from aqueous solutions is discussed.

To summarize the theoretical part of this thesis it is worthwhile to note that the Author studied carefully the research subject with critical view, and used appropriate number of

bibliography sources. It is evident fact that Iwona Lupul gained a deep understanding of the theoretical knowledge and the discussed problems.

After the literature review, chapter III presents the aims and motivations underlying the doctoral dissertation. The main objective is to study the adsorptive removal of organic and inorganic toxic compounds from aqueous solutions on agricultural by-products-based activated carbons.

The next, rather short, chapter IV is devoted to the description of the materials and methods used. At first, activated carbon precursors (hemp stem, and palm kernel shell) as well as selected adsorbates (atrazine, Congo red, methylene blue, cyanocobalamin, and hexavalent chromium) are presented. Then, in the appropriate order, methods of activation, methods of modification of the surface chemistry of activated carbons, adsorption runs from aqueous solutions and characterization of precursors and activated carbons are discussed.
In chapter IV, the last three subchapters are incorrectly numbered. 4.1, 4.2 and 4.3 should be replaced with 4.4, 4.5 and 4.6.

The next part of the dissertation (chapter V – the longest one, over 60 pages in volume) is focused on results and discussion. It begins with a short presentation characterizing agricultural precursors of activated carbons, i.e. hemp stem, and palm kernel shell. In the next subchapter 5.2 the effects of various methods of precursors activation on porous structure development in the resulted activated carbons are presented and discussed. The type of precursor, type of activating agent, process conditions are taken into consideration. For all obtained activated carbons, low-temperature nitrogen adsorption isotherms are determined as well as an elemental analysis (C, H, N, O) is performed. Calculated parameters characterizing the porous structure, such as specific surface area BET, micro- and mesopore volumes, pore size distribution are considered and correlated with activation method and precursor properties. More than thirty activated carbons have been produced, but mainly from hemp stem. In the case of selected activated carbons, a chemical modification of their surface was performed (subchapter 5.3). Various modifying agents as well as process conditions were used for particular activated carbons. Twelve modified activated carbons samples were obtained. Effects of modification were investigated and compared with use of various methods: elemental analysis, FTIR spectroscopy, XPS spectroscopy, and temperature programmed desorption (TPD).

In the next three subchapters (5.4, 5.5 and 5.6), results of adsorption experiments with the use of the chosen modified and unmodified activated carbons and additionally one

commercial activated carbon Organosorb 10 CO (DESOTEC) are presented, compared and discussed.

In the first of these subchapters the results of atrazine adsorption on microporous hemp stem-based activated carbons are presented. Adsorption kinetics is better described by the pseudo-second-order kinetic model in comparison with first-order and intraparticle models. The equilibrium experimental data are best fitted by the Langmuir-Freundlich or Langmuir models. The influence of activated carbons surface chemistry and pH solution is analyzed. A mechanism of atrazine adsorption is proposed. Next subchapter 5.5 is dedicated to the adsorption of three high molecular organic compounds (methylene blue, Congo red, cyanocobalamin) on hemp stem-based activated carbons. The best adsorption description gives a pseudo-second-order kinetic model and - in the case of adsorption equilibrium – the Langmuir model. The effect of adsorbate is examined in detail. In the case of methylene blue, the effects of porous structure and surface chemistry of activated carbon were analyzed in greater detail. The last investigated adsorption system was comprised by Cr(VI) ions adsorbed on palm kernel shell-based activated carbons. The effects of solution pH and surface chemistry of activated carbons were taken into account. Activated carbon was modified using various methods. Organosorb commercial carbon was also used for comparison. The best description of adsorption kinetics gave a pseudo-second-order model, and the adsorption equilibria Langmuir model. A mechanism of Cr(VI) adsorption was proposed. XPS measurements also proved to be very useful for this purpose.

At the end of the dissertation, general conclusions of the performed research were described. This whole chapter is divided into seven groups of detailed conclusions. It has been shown that both used precursors and various activation methods give the possibility of obtaining activated carbons with a strongly differentiated porous structure. Using different modification methods (various agents and process conditions) allows to vary the carbon surface chemistry in a wide range. Atrazine adsorption investigations revealed that surface functionality had a significant influence on the activated carbon behavior in this process. Activated carbons prepared by H_3PO_4 activation of hemp stem had mesoporous character and were good adsorbents for methylene blue. Subsequent annealing in nitrogen and hydrogen atmospheres gave different surface chemistry of these activated carbons. The pore volume distribution was similar. The more basic surface of hydrogen-treated carbon reduced the methylene blue adsorption. This activated carbon allowed to study the effect of different molecular size of used organic adsorbates (methylene blue, Congo red and cyanocobalamin)

on their adsorption. The chemically modified palm kernel shell-based activated carbons were found to be suitable adsorbents for the removal of hexavalent Cr from aqueous solutions.

These carbons had strongly differentiated surface chemistry and similar porous structure. The basic surface character enhances the removal capacity towards Cr(VI). The strongly acidic nature of the surface caused a lower sorption capacity.

The main objectives of the paper have been fulfilled. The results are well presented and their interpretation is at a high scientific level. All experiments are well arranged and measurements techniques and methods are correctly applied. It is noteworthy that the wide spectrum of the studied issues implements new research ideas.

However, there are some remarks and comments related to the text that should be explained in detail.

1) On page 12 in subchapter 2.3. Activated carbon – paragraph 2.3.1. Microstructure and pore structure should be inserted, and the existing paragraph 2.3.1. Chemical structure of activated carbon should be renumbered as 2.3.2.

2) In VII. References - in position 35. the name of the first author is Jankowska not Jasińska and - on the other hand - it would be better to use a newer version of this monograph (in English) H. Jankowska, A. Świątkowski, J. Choma, Active carbon, Ellis Horwood Limited, New York 1991.

3) In VII. References - position 65. should be written as follows: L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, Carbon materials as adsorbents in aqueous solutions, *in* "Chemistry and Physics of Carbon", Ed. by L.R. Radovic, Vol. 27, Marcel Dekker, Inc., New York- Basel 2001.

4) In VII. References - in two cases the same article: positions 66 and 193 as well as 202 and 221, respectively, is quoted twice.

The above comments do not affect the thoroughly positive evaluation of the entire dissertation.

In my opinion, the reviewed thesis fulfills all requirements set on theses aimed for obtaining a Ph.D. degree.

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