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SUMMARY OF HABILITATION THESIS

The content of the habilitation thesis is structured in five chapters and presents the main original scientific results in Environmental Engineering field published by me and obtained after conferring the PhD title according to the Order of the Minister of Education and Research no. 3876 / 19.05.2004. In addition, the paper presents the research directions that I focused my activity on during this period, as well as the strategy that I proposed to approach in the next period, but also in the medium and long term, in terms of my academic and scientific development.

In the *first chapter* of the work, I presented my academic, but especially scientific, evolution, starting from 2004 and up to now. Thus, during this period I promoted from assistant professor to associate professor. The evolution in the teaching career was supported by the scientific research activity materialized by the publication of 39 articles in national and international journals (of which 29 in ISI listed journals), as first author, corresponding author or co-author, 30 of papers communicated at national and international conferences, as well as 42 research contracts, development of human resources or infrastructure contracts. Of these, I was contract director at 6 of them.

The second chapter presents the achievements obtained in the research activity regarding the use of different adsorbent materials for the removal of organic or inorganic pollutants from waters.

Thus, it was studied the retention of phenol, respectively, *p*-nitrophenol on activated carbon obtained from biomass-type raw materials (coffee grounds, respectively, fir sawdust). It was evaluated the adsorptive performances of the four prepared materials using several mathematical models that allowed the determination of their maximum adsorption capacities, the making of predictions on the mechanism by which polluting species are retained on the surface of the adsorbents, but also a kinetic evaluation of the adsorption processes. The adsorption of phenol on activated carbon obtained from coffee grounds takes place in the monolayer, through interactions of a physical nature attributed to the p-p interactions between the electrons of the aromatic rings in the phenol structure and the electrons of the graphitic structure. From a kinetic point of view, the pseudo-second-order model best fits the experimental data. Regarding the adsorption of *p*-nitrophenol on activated carbons obtained from fir sawdust, it was found that depending on the activation agent used to obtain them (acid, base or salt), the way the process unfolds differs, proceeding in a monolayer on the adsorbent activated with a base and in the multilayer on the one activated with a salt. The latter adsorbent showed the best adsorption capacity, which can be attributed to the basic nitrogen-containing functional groups as well as the graphitic structure because both structures show a good affinity in terms of π-π interactions with the aromatic rings of the molecules of *p*-nitrophenol.

As adsorbent material was used commercial granular activated carbon for the retention of *p*-toluidine and *p*-cresol, respectively. Kinetic studies showed that the pseudo-1st order kinetic model adequately describe the adsorption process of *p*-toluidine by this material, the acidic groups

on the surface highlighted by Boehm titration favoring the adsorption of *p*-toluidine. Regarding the adsorption kinetics of p-cresol, the kinetic data were best fitted by the Avrami model, the values of the fractional order n in this model (close to 1) indicating that the adsorption of *p*-cresol is best described by first-order kinetics 1, as in the case of *p*-toluidine. Regarding the adsorption mechanism of *p*-cresol, the results indicate that film diffusion and intragranular diffusion are competing in the overall control of adsorption that is physical in nature and occurs mainly, through π–π interactions and electron-donor mechanism.

The use of adsorbent materials obtained from biomass also gave good results in the case of retaining inorganic pollutants such as ammonium or nitrates, for which a natural zeolitic tuff of the clinoptilolite type (for ammonium) and activated carbon prepared from black tea leaves (for nitrates) were used. Regarding ammonium retention, a modification of the natural tuff considerably improves the performance of the adsorbent material. For nitrate retention, were tested two materials obtained from black tea leaves: one was prepared by boiling the leaves, followed by drying, and the other further calcined at 400°C. Experimental data fitted with Langmuir, Freundlich and Temkin models allowed the calculation of maximum adsorption capacities with close values. The data obtained best fitted by the Freundlich adsorption isotherm indicating multilayer physical adsorption. In addition, the application of regeneration cycles with HCl, NaOH, and Na_2CO_3 solutions, respectively, demonstrated that a number of three cycles for each individual material almost completely restores the adsorption capacity of the two adsorbents.

In the *third chapter*, it was studied the possibility of reducing environmental pollution by applying treatments to products that during or after use contribute to environmental pollution. Following the application of these treatments there are changes in the structure or composition of these products, which have the effect of reducing the polluting impact on the environment.

Thus, it was studied the obtaining of some alkyl-benzenes on phosphotungstic acid (HPW) catalysts supported on mesoporous silica (SBA-15). Such products have a reduced toxicity and various uses in industry. The raw material used was m-cresol. The main advantage of the catalyst is that no major side reactions, such as oligomerization or dialkylation occur. It was obtained 1-decene dimers with a maximum yield of 2% and the polyalkylation of m-cresol occurring to a small extent (yield of max. 10%).

Another aspect addressed was that related to the hydrodesulfurization of thiophene and benzothiophene in the presence of Co-Mo-Re catalysts supported on γ-Al_2O_3 and mesoporous silica supports, taking into account that the removal of sulfur from fuels is one of the main priorities for protecting the environment against acid rain. Thus, the presence of HMS mesoporous silica causes a decrease in the acidity of the CoMoRe/γ- Al_2O_3 catalyst and an increase in the textural properties value. On the other hand, these characteristics of both catalysts decrease after sulfurization, due to the larger volume of the sulfur atom compared to the oxygen it replaced. Pressure and temperature similarly influence the performance of the hydrodesulfurization process on the two catalysts. The presence of HMS-type mesoporous silica reduces the performance of the CoMoRe/γ-Al_2O_3 catalyst, probably due to the negative influence on the concentration of acid centers or the structure of the HMS and the catalyst-support interaction. The thiophene hydrodesulfurization process was also studied on the Mo-Co-Ni/γ- Al_2O_3 catalytic system where its stability was evaluated over a 2-hour time period when it was observed that the loss of catalytic activity of the catalyst was approximately 4% in the first 30 minutes, but after 40 minutes after the

start of the test, it remained almost constant. For the hydrodesulfurization of thiophene we proposed a kinetic model based on the Langmuir-Hinshelwood theory, which indicates a proper conversion of thiophene, the values of the kinetic parameters being close to those proposed for hydrotreating processes.

The *fourth chapter* of the work refers to obtaining renewable fuels starting from different raw materials and in the presence of different catalytic systems.

The use of natural compounds in the manufacture of liquid fuels can present disadvantages even from the point of view of environmental pollution, because of either the high viscosity that causes incomplete combustion, or the high oxygen content that limits the concentration of these components in the fuel. In this way, we studied the process of hydrodeoxygenation / hydrocracking of oxygenated compounds such as methyl esters of fatty acids from palm oil, using a bifunctional catalyst containing a metal function based on copper and palladium and an acidic function of the ZMS-5 type. The tested catalyst was the CuPd/γ-Al_2O_3–ZSM-5 catalyst which allowed the obtaining of n-alkanes, iso-alkanes, saturated cyclic and aromatic hydrocarbons with 9 to 18 carbon atoms, finding that the cyclization and aromatization reactions are favored by increasing temperature.

Another study focused on the hydrotreating process of methyl oleate on the Ni-Mo/γ-Al_2O_3 catalyst, using a combination of Zn-ZSM-5 and γ-Al_2O_3 supports, in two- and even three-layer catalytic systems. We found that three-layer catalytic systems enhance the formation of n-paraffins, mainly C17 and C18, which are important diesel components.

The influence of treatment with polyethylene glycol 4000 (PEG 4000) on the main characteristics of 58S bioglass was evaluated, it being known that bioglass is a new biomaterial that has various uses, including in the packaging industry but also in cosmetics, provided to present a low degree of crystallinity. The study demonstrated that treating bioglass with PEG 4000 makes its use in the cosmetic industry safer by eliminating the risk of crystalline structures, without significant changes in other characteristics.

In the *fifth chapter*, I presented a proposal for the evolution and development of the academic and scientific career. This aims, on the one hand, to form a doctoral school in Environmental Engineering within IOSUD from UPG Ploiești, but also to strengthen links with schools with the same orientation from universities in Romania or abroad. The development of the scientific career takes into account the development of the research directions approached so far but also the opening to new ones. The main directions to be addressed with the future PhD students, as well as with the members of the research teams, will focus on the following aspects:

- optimizing the performance of adsorption processes, both in terms of the conditions for the synthesis of bioadsorbents, with an emphasis on the combination of different raw materials with complementary properties, as well as the mutual influence of inorganic and organic pollutants;
- studying water depollution by combined adsorption and photocatalysis techniques;
- utilization of the liquid fractions obtained simultaneously with the bioadsorbents in the biomass pyrolysis processes.

Together with my team, I will materialize the research results in publishing papers, participating in scientific conferences and realizing research grants with academic and industrial partners.