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HABILITATION THESIS SUMMARY

Sorption - Separation Method of Chemical Compounds from Aqueous Media

The habilitation thesis, presents in concise form the results obtained in the main experimental direction of research activity carried out throughout my 25 years of activities within higher education. The sorption of organic substances, the theme I chose when enrolling in my own PhD in 1992, remained my first choice ever since.

As I said in 1998, it has opened "work perspectives" for many years, firstly by evaluating the sorption properties of some new types of natural or synthetic materials in the uptake of organic dyes from aqueous solutions and, secondly, by expanding the environmental and biotechnological applications of the sorbents functionalized with reactive dyes.

The separation and concentration methods underlie the most important techniques for recovering useful micro components of technological interest, for the isolation of impurities or harmful compounds from industrial or natural samples, for the bio-control and monitoring of biotechnological processes, but also for ensuring the environmental protection or the rigorous quality control of products**.** The separation methods can be independent steps in technological processes or part of complex procedures performed on flow or in the laboratories of analysis and quality control of finished products, named combined methods (analytical methods in several steps which must optimally combine the sampling and sample preparation with weighing, solubilisation, concentration and determination).

A complex method of separation, *Sorption* can be defined as the totality of interactions that generates reversible or irreversible associations, which ensures the retention of a chemical species (*sorbate*) from a gaseous or liquid

phase, on a solid or liquid material, named *sorbent*. It underpins the development of more efficient combined methods (concentration - separation - identification - determination) of analysis (*e.g.* advanced chromatographic techniques: HPLC or GC) of chemical compounds from various types of matrices, with interest in environmental protection, biotechnology, biological and clinical areas, and different other technological processes.

However old, the ***Sorption*** *represents even now a viable alternative* to other methods of separation due to its *major advantages* appreciated *in terms of efficiency and cost*: increase of process sensibility; increase of selectivity; reduction of matrix effects; possibility of simultaneous achievement of pre-concentration and the proper estimation. But the great advantage of this method is the possibility to use as sorbents many classes of materials: synthetic to natural low-cost materials (natural as well as wasted materials from different industries and agriculture) as suitable sorbents for decolourization of industrial effluents.

A. Of the many organic compounds I have considered for study the sorption of ***organic dyes***, detailed in *Chapter 2* of the habilitation thesis.

Optimization of dyeing (tinctorial) processes, use of some unconventional methods related to this topic, as well as modification of cellulose fibers by cationization have brought into focus the studies concerning the sorption of dyes onto different supporting materials, expanding the area of scientific interest from analytical chemistry and physical chemistry to technological issues. The sorption of dyes, as the initial stage of the dyeing process was mainly investigated in order to elucidate the physico-chemistry of the interactions between dye and textile fiber, but also for their removal from the waste water resulted from the complex process of chemical finishing of textile fiber, in the context of the sustainable development principle: the polluter pays.

The negative impact due to the presence of dyes in wastewater is not only because their color, but especially because of the effect of preventing the penetration of sunlight and water oxygenation inhibition, which could pose a threat to aquatic life. Moreover, many of the dyes released break down into toxic, carcinogenic or mutagenic chemical products, *such as benzidine, naphthalene and other aromatic compounds*.

Experimental studies carried out in this direction in static/dynamic systems, have targeted the use of an extremely wide range of adsorbent materials:

- *synthetic* (ion exchange resins such as Amberlite IRA-401S, Vionit AT-1, Purolite A-400, A-500, C-100, C 145, C107E, polyamide, celluloses ion exchange (DEAE, TEAE, ECTEOLA, AE, GE, P), adsorbent celluloses as CELLETS, active charcoal.
- *local natural*: peat from Poiana Stampei, seashells of *Rapana Venosa* from Black Sea,
- *agro-industrial waste* (corn cob, pumpkin core, sun flower seed shells, apple seed, citrus seed),

- *industrial* waste (sawdust, lignin, cellolignin, ash and modified ash, dead biomass and dead biomass immobilized on alginate , textile fiber waste (hemp, polyacrilonile).

All these materials were used as sorbents to remove different types of dyes from aqueous media: BRed – reactive Red Briliant HE-3B; BMEB – Blue reactive M-EB; RV – Reactive Violet 5; RO – Reactive Orange 16; MB – Methylene Blue (Basic Blue 9 – BB 9); RB – Rodhamine B; CV – Cristal Violet/ MV – Methyl Violet.

Research carried out mainly in batch system and in unicomponent solutions followed the:

- influence of operational parameters (temperature, dye concentration, sorbent dose, contact time, presence and concentration of electrolytes, stirring) and those dependent on sorbent (structure, porosity, physico-chemical transformations applied, functional groups) or on the type of dye;
- the study the equilibrium of sorption in order to determine the characteristic quantitative parameters using the literature isotherms models (Freundlich, Langmuir, Dubinin-Radushkevich, Temkin);
- the kinetic and thermodynamic modeling of sorption, absolutely necessary in technological approaches of ecological and biotechnological interest. The results had the purpose of establishing the global thermal effect, thermodynamic parameters that provide the initial information on the type of mechanism, setting the rate limiting step and the type of diffusion that underlies the mechanism of the process;
- physical-chemical characterization of sorbent before and after sorption;
- desorption studies and regeneration of some sorbents;
- ways of using sorbents loaded with dyes;
- different preliminary studies, conducted in collaboration, in order to optimize the sorption process and apply this methodology to the real industrial effluents.

It should be noted that preliminary studies on the use of unconventional sorbents (pumpkin core and corn cob) started during the doctoral training but were continued and extended with a range of these types of materials (natural or synthetic) with adsorbing properties.

Furthermore, the study of sorption equilibrium was extended by applying some new models (Tempkin, Dubinin-Radushkevich, Elovich) compared to the initial ones (linear model, Freundlich and Langmuir) and was completed with more complex elements of thermodynamics and kinetics, absolutely necessary to technological approaches with ecological and biotechnological interest. Thus, the thermodynamic modeling involved the calculation of the thermodynamic characteristics parameters (ΔG, ΔH, ΔS), and additionally calculating the isosteric heat of reaction by using the Clausius-Clapeyron equation, and in the case of the kinetic modeling of equilibrium we

have gone from Fick's laws to the Lagergren, Ho and Elovich models, models about diffusion mechanism (Weber and Morris model, McKay model, Boyd-Reichenberg model), respectively to the calculation of activation energy for the sorption process based on the Arrhenius equation.

The structure of new materials as well as dye-sorbent interactions have been studied with modern methods of physical and chemical characterization: scanning electron microscopy–SEM; X-ray diffraction; energy-dispersive X-ray spectroscopy (EDX); Fourier Transform Infrared Spectroscopy (FTIR); thermo-gravimetric methods, determination of particle size distribution by measuring the porosity or specific surface determination by method Brunauer-Emmett-Teller (BET).

B. Another direction of research, whose results are summarized in *Chapter 3* of my habilitation thesis refers to the use of reactive dyes as ligands for new types of sorbents with increased efficiency for retention of cations of heavy metals or for obtaining of macromolecular supports functionalized used in affinity chromatography or bioaffinity with immobilized metal for biomacromolecules separation or separation and / or concentration of products obtained through biotechnological processes.

The efficiency of functionalized cellulose as sorbent materials for proteins and enzymes (casein, lysozyme and α-amylase) in low concentrations has been confirmed by experimental data and by the values of some characteristic parameters (sorption capacity, Langmuir equilibrium constant, variation of Gibbs free energy). These data constituted, at the time of sustaining the doctoral thesis, interesting original results, opening the prospect of further investigation of interdisciplinary interest, and this has happened by extending the sorption studies to test the adsorbant potential of some cellulosic sorbents functionalized with dyes and metal ions. Attention is given to the study of interactions sorbent - dye and sorbent - dye - protein by infrared spectroscopy, being noticed important changes in the domain of the absorption bands influenced by the formation of intramolecular and intermolecular hydrogen bonds.

Chapter 4 of habilitation thesis shows some directions that will be approached in the future research work. In order to develop a strategy for the research activity I took into consideration the total achievements from all research directions approached in over 25 years of activity, because I am here due to each of them. It should be noted that that among these "sorption - method of separation" remained the main research direction until today.

Because I believe that true academic professional development must consider the following four areas:

(1) professional;

(2) educational/teaching;

(3) scientific research;

(4) participation in academic life research will be conducted, as before, by combining teaching activities, work with students, involvement in academic community and personal life.

The future strategy is based on a series of general objectives :

- Continue to participate in competitions launched for projects and national research programs by submitting proposals as project manager/director of a workgroup, or to become member in research groups that submit research proposals;
- Continue to capitalize the research results by publishing scientific papers in ISI, BDI and CNCSIS journals, as well as by participating in national and international scientific meetings.
- Translate topics of dissertation theses into research directions within the doctoral program.
- Attract students from the master program in research activities and PhD programs.
- Contribute through my entire activity to increase the national and international exposure of the department / faculty / doctoral school / university and research center.

The following major research directions will be taken into consideration:

➢ Extension study of the sorption separation process by:

– The identification, characterization and evaluation of the sorption performance of new materials in order to capitalize them as sorbents for retention with high efficiency of some other organic species.

– Approach the dynamic sorption of organic substances from aqueous media;

– Extend the study of sorbent functionalized with dyes;

– Expand sorption studies by considering the mixtures bi - and multi dyes/organic compounds

– Expand sorption studies to the real systems;

– Study of desorption process and the release of active compounds in controlled conditions.

➢ Integration of the sorption in technological processes and the development of other useful techniques for separating and/or concentration of pollutant organic compounds or compounds with medical, food, pharmaceutical or cosmetic interest.

➢ Also, I think that it is desirable and useful to approach again and develop the research directions that have been conducted in the past (product quality, university management, other methods of separation and bio-separation).

The development of my research activity will take into account a new aspect, which refers to the fact that I was granted the Habilitation Certificate that offers me the possibility to contribute to the formation of researchers through a doctoral program, respectively the education and training aspect.

In this direction I will aim to develop skills and competences necessary for a future scientist in our future researchers, whether the applicants intend to work in education, research institutes, private research and development companies. *These skills and competences include, among others, reliability, perseverance, curiosity, loyalty, systematization, dreaming, troubleshooting, performance orientation, development in individual or team work, regardless of the research topic.*

My final goal is to form a team, starting from one researcher, where people will work successfully together or at long distance one from other, with or without the daily presence of a supervisor, in a modern laboratory, not only by involvement in a research program required (Ph.D., post-doctoral), but also by working simultaneously in different teams.

My strategy for the future development of the scientific research presented in Chapter 4 includes only a few directions, because meanwhile, other new directions will certainly appear, that are in accordance with the trends from this field, with the established partnerships, with development of the society or separation techniques, with physico-chemical characterization

In addition, I think that it is desirable and useful to approach again and to further develop the research directions that have been conducted in the past (product quality, university management, other methods of separation and bio-separation).

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