HABILITATION THESIS

Nanostructured Oxide Materials and Functionalized Materials with Applications in Environmental Protection

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ABSTRACT

The habilitation thesis entitled "Nanostructured Oxide Materials and Functionalized Materials with Applications in Environmental Protection" is a synthesis of the scientific activity that I have carried out after defending my PhD thesis in 2004.

The scientific research activity that is the subject of this thesis was directed towards the synthesis and characterization of two types of materials: nanostructured oxide materials and materials functionalized by impregnation with various extractants. Some of the materials obtained have been tested in environmental applications. These have been successfully used for the adsorption of dyes and metallic ions from dilute aqueous solutions, in view of applying these processes either for treating wastewater or for recovering valuable chemical species.

The habilitation thesis is structured in two parts, and is based on 28 personal scientific papers (14 as lead author), of which 24 published in ISI ranked journals and 4 published in journals indexed in other international databases.

In the ***first part of the present thesis*** are presented the main professional, scientific and academic achievements obtained after I defended my PhD thesis.

A sustainable solution to the problem of continuously increasing water demand is the treatment of contaminated water. Adsorption is a widely used technique for advanced wastewater treatment, especially for the removal of those pollutants that can not be easily biodegraded. Current research in the field of water treatment aims at developing new materials with advanced adsorbent properties. Starting from this idea, the research activity presented in the first part of the thesis had as purpose the synthesis, characterization and evaluation of the applicative potential of such materials.

Nanostructured metal oxides are considered promising materials, especially for use as adsorbent materials for the removal of heavy metals, arsenic species, dyes and other organic pollutants from aqueous systems.

For the synthesis of nanostructured oxide materials, the thermal decomposition of carboxylate complexes (precursor) was used. This method produces oxide powders with nanometric particles at relatively low temperatures, with a yield of practically 100 %. Carboxylate precursors were obtained by the redox reaction between metal nitrates and polyols. The decomposition of carboxylates at relatively low temperatures (300-350 °C) led to

single/mixed oxide mixtures with high reactivity. By calcining them at suitable temperatures, the oxide systems with the desired compositions were obtained. With this new method, several spinel oxide systems with nanometric particles were prepared: ferrites MFe_2O_4 (M = Co, Cu, Ni, Zn), maghemite γ-Fe_2O_3 and zinc aluminate $ZnAl_2O_4$.

In the case of magnetic systems, magnetic properties were correlated with the temperature of the thermal treatment and their composition. In the case of maghemite, the residual carbon generated by the decomposition of the polyol (polyethylene glycol) acts as insulator and prevents the agglomeration of the oxide nanoparticles, influencing the magnetic properties of the powder. ZnO-Zn_2SiO_4-SiO_2 nanocomposites having different compositions and properties were prepared by the sol-gel method modified by an original procedure, involving the thermal decomposition of Zn (II) carboxylates dispersed in the pores of silica gel.

Cobalt, copper, nickel and zinc ferrites have been tested for adsorption of Congo red dye from aqueous solutions, and have proven to be materials with remarkable adsorbent properties. Although zinc ferrite has a higher adsorption capacity, cobalt, copper and nickel magnetic ferrites have the advantage of being easily separated from the treated solution by the application of a magnetic field.

In view of improving their adsorbent properties, magnesium silicate and Amberlite XAD7 resin have been functionalized with extractants containing nitrogen, phosphorus and sulfur functional groups (tetrabutylammonium dihydrogen phosphate, tetraethylammonium bromide, sodium β-glycerophosphate, and thiourea), which are considered “green”, being environmentally friendly. Several methods have been used for the functionalization by impregnation, the most effective being the pellicular vacuum solvent vaporization, which was applied for the first time for this purpose.

The so-functionalized materials were used for the adsorption from aqueous solutions of rare metals ions: Eu (III), La (III) and Nd (III). Experimental results have shown that these are effective adsorbent materials, with remarkable efficiency. Moreover, these materials have the advantage that they have been obtained by easy and non-polluting methods.

In order to establish the mechanism of formation and decomposition of carboxylates, to characterize the materials obtained and to evaluate their performance in adsorption processes, different techniques of analysis were used: thermogravimetric analysis (TG), differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy

(TEM), energy dispersive X-ray analysis (EDX), specific surface area measurements (BET), ultraviolet and visible spectrometry (UV-Vis), inductively coupled plasma-mass spectrometry (ICP-MS).

To determine the adsorbent properties of these materials as well as the adsorption mechanism, studies on pH influence, kinetic studies, equilibrium studies and thermodynamic studies were performed.

In the ***second part of the habilitation thesis*** are presented the plan of evolution and development of the professional, scientific and academic career, the proposed objectives and the future research directions.

At the end of the habilitation thesis are given the 246 references cited.