

**Obtaining advanced materials with applications in wastewater purification through  
superior recovery of some waste**

pentru obținerea titlului științific de doctor la  
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## CHAPTER I

### **GENERAL CONSIDERATIONS ON ADSORPTION AND TYPES OF ADSORBENTS USED FOR WASTEWATER TREATMENT**

This chapter presents i) adsorption as a wastewater treatment method; ii) the classification of the types of adsorption, iv) the main parameters that influence the adsorption process, and the advantages of the adsorption processes; v) kinetics, vi) adsorption isotherms. Following is the presentation of the main methods of water pollution, the classification of adsorbents, and a brief presentation of each category of adsorbents. The chapter concludes with the main applications of the adsorption process to water remediation, respectively emergent pollutants, dyes, and heavy metals.

## CHAPTER TWO

### **METHODS FOR THE CHARACTERISATION THE COMPOSITE ADSORBENT MATERIALS**

This chapter presents the analytical methods used for the physicochemical properties of the adsorbents, namely i) BET, ii) scanning electron microscopy (SEM and EDAX); iii) transmission microscopy (TEM/HRTM); iv) Atomic force microscopy (AFM), v) X-ray diffraction spectroscopy techniques; vi) FT-IR spectroscopy; vi) spectrophotometric (UV-Vis), vii) thermal analysis (TG, DTA, DTG), viii) scanning calorimetry, the principle of the analysis method, and the equipment used in this thesis.

## CHAPTER THREE

### **PERFORMANCE EVALUATION OF DIFFERENT ADSORBENTS FOR PHOSPHORUS REMOVAL FROM WASTEWATER**

This chapter presents the first comparative assessment of three different types of materials (magnetic, semiconductors, and composite) as environmentally friendly, cheap adsorbents for phosphorus removal from wastewater versus two conventional chemical reagents used currently for phosphorus precipitation in wastewater treatment plants. Several experiments were done to investigate the influence of adsorbent type, dosage, and contact time on the efficiency of the processes. The adsorption process was fast and equilibrium was reached within 150 min. We found that the phosphorus adsorption efficiency of these materials was higher than the chemical method. The obtained results indicate that the specific surface area directly influences the performance of the adsorption process. EDS analysis was used to analyze the adsorbent composition and analyze the type and content of elements in the substrate before and after the reaction with wastewater.

## **CHAPTER FOUR**

### **USE OF WASTE MIXTURES FOR THE DESIGN AND DEVELOPMENT OF A HIGHLY EFFECTIVE ADSORBENT FOR THE REMOVAL OF CADMIUM FROM AQUEOUS SOLUTIONS**

Chapter four presents The study designed to investigate the development of a newly engineered adsorbent by functionalizing two different types of waste (industrial and food) with magnetic nanoparticles as environmentally friendly, highly efficient, cheap material for cadmium removal from aqueous solutions. This nano-engineered adsorbent (EFM) derived from waste eggshell and fly ash was used to remove the cadmium from the aqueous solution. SEM analysis has demonstrated that magnetite nanoparticles were successfully loaded with each waste. In addition, was obtained a double functionalization of the eggshell particles with ash and magnetite particles. As a result of this, the EFM surface area substantially increased, as confirmed by BET. A comprehensive characterization (BET, FT-IR, SEM, XRD and TGA) was performed to study the properties of this newly engineered adsorbent. Batch experiments were conducted to investigate the influence of different reaction parameters: temperature, pH, contact time, dosage adsorbent, initial concentration. Results showed that cadmium adsorption reached equilibrium in 120 min., at pH 6.5, for 0.25 g of adsorbent. The maximum efficiency was 99.9%. The adsorption isotherms research displayed that the Cd<sup>2+</sup> adsorption fitted on the Freundlich model indicated a multi-molecular layer adsorption process. In addition, the thermodynamic study ( $\Delta G < 0$ ,  $\Delta H > 0$ ;  $\Delta S > 0$ ) shows that cadmium adsorption is a spontaneous and endothermic process. The adsorbent kinetic study was described with the pseudo-second-order model indicating a chemisorption mechanism. Desorption results showed that the nano-engineered adsorbent (EFM) can be reused. These data confirmed the possibility to enrich relevant theoretical knowledge in the field of waste recovery for obtaining newly designed adsorbents, performant and inexpensive for wastewater remediation.

## **CHAPTER FIVE**

### **USE OF EGGSHELL WASTE TO DESIGN AND OBTAIN HIGHLY EFFICIENT ADSORBENTS FOR NICKEL REMOVAL FROM AQUEOUS SOLUTIONS**

In the fifth chapter, using an innovative approach to remediating metal-polluted water, was developed a study where the eggshell waste was used to prepare two new low-cost nanoadsorbents for the retrieval of nickel from aqueous solutions. Scanning electron microscopy (SEM) results show that in the first eggshell-zeolite (EZ) adsorbent, the zeolite nanoparticles were loaded in the eggshell pores. The preparation for the second (iron(III) oxide-hydroxide)-eggshell-zeolite (FEZ) nano adsorbent led to double functionalization of the eggshell base with the zeolite nanoparticles, upon simultaneous loading of the pores of the eggshell and zeolite surface with FeOOH particles. Structural modification of the eggshell led to a significant increase in the specific surface, as confirmed using BET analysis. These features enabled the composite EZ and FEZ to remove nickel from aqueous solutions with high performance and adsorption capacities of 321.1 mg/g and 287.9 mg/g, respectively. The results

indicate that nickel adsorption on EZ and FEZ is a multimolecular layer, spontaneous, and endothermic process. Concomitantly, the desorption results reflect the high reusability of these two nanomaterials, collectively suggesting the use of waste in the design of new, low-cost, and highly efficient composite nanoadsorbents for environmental bioremediation.

## **Chapter six**

### **FINAL CONCLUSIONS**

The sixth chapter presents the conclusions of the thesis structured on each of the three experimental studies developed and presented, as well as the future perspectives of the doctoral student from the perspective of completing the doctoral thesis.

The thesis ends with an up-to-date bibliographic list.