BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 64 (68), Numărul 1, 2018
Secţia
CHIMIE şi INGINERIE CHIMICĂ

HABILITATION THESIS SUMMARY

Heavy Metals Removal from Wastewaters by Sorption Processes

Abstract. The habilitation thesis presents the most significant results of the researches oriented towards polymeric materials (organic synthetic resins and polyurethane foams) and waste materials as sorption media for heavy metal ions. Some new chelating sorbents have been prepared by covalent immobilization of desired groups, also by some special, noncovalent methods. The proposed polymer sorbents have enhanced efficiency and good selectivity towards targeted precious and toxic heavy metal ions. Some indigenous wastes (hemp, rapeseed, Romanian pine bark, fly ash) have been investigated as potential sorbents for Cu(II), Cd(II),Zn(II), Pb(II) ions. The obtained results of are significant for the future development of the tested wastes into beneficial materials for industrial and environmental applications.

The habilitation thesis “*Heavy Metals Removal from Wastewaters by Sorption Processes*” is an overview of the professional, academic and scientific activity performed at the “Cristofor Simionescu” Faculty of Chemical Engineering and Environmental Protection, Department of Engineering and Environmental Management in the post-doctoral period (1998-2017).

The thesis represents an integrated approach of the leading scientific contributions to the following research directions:

- sorption removal/recovery of heavy metal ions by using polymeric materials (organic synthetic resins and polyurethane foams);
- studies concerning the feasibility of the industrial and agricultural wastes conversion into value-added sorbents, applicable in the advanced wastewater treatment;

➢ the adaptation and development of analytical methods for the determination of chemical species in low concentrations.

The results of the scientific activity are embedded in the chapter 2 of the habilitation thesis, under the name of **"Retention of heavy metal ions from aqueous solutions by sorption on functionalized polymers and waste materials".** In turn, chapter 2 is structured in 3 main sections.

Section 2.1.

After an emphasis on the imperative of heavy metals removal from aquatic environments (2.1.1.), the sorption methods (2.1.2.) and the main types of sorbents (2.1.3.) are described and characterized. A special interest has been shown for polymeric (2.1.3.1.) and waste materials (2.1.3.2.) as sorption media for heavy metal ions. A distinct reference is made to the sorbents targeted in the research work (chelating resins, polyurethane foams, hemp wastes, rapeseed wastes, pine and silver fir bark wastes, fly ash) and their choice is rigorously justified is made in 2.1.4.

Section 2.2.

This section is directed towards the studies concerning the development and implementation of new selective **sorbents** based on **chelating polymers** (2.2.1.**)** and **polyurethane foam** (2.2.2.*)* to target precious and toxic heavy metal ions (Fig. 1). The targeted issues are related to:

– preparation and properties of new chelating sorbents with improved performances;

– investigating the effectiveness of the developed polymers under various experimental conditions (solution pH, metal ion concentration, sorbent dose, contact time and temperature);

– modeling the heavy metal sorption process (isothermic, kinetic and thermodynamic models);

– the use of these new chelating sorbents in selective processes of precious heavy metal recovery;

– the applicability of these resins in the removal of toxic heavy metals ions from industrial effluents;

– development of new methods of analysis which combine the concentration of precious metal ions from aqueous samples with their subsequent determination directly in the resin phase.

Fig. 1 – Focus on the studies concerning polymeric materials as sorption media.

The results of researches dealing the *sorption removal / recovery of heavy metal ions by using polymeric materials* have been published in 30 papers of which 11 ISI papers and 19 papers published in BDI journals. The research direction targets to the adaption and development of analytical methods for the determination of chemical species in low concentrations is supported by the 7 published articles: 3 (1 as sole author) in ISI journals and 4 papers published in BDI journals.

2.2.1. *New Chelating Polymers as Selective Sorbents of Heavy Metal Ions*

After some general considerations (2.2.1.1.), the relevant results are presented in the next succession:

2.2.1.2. *Chelating sorbents with grafted groups*

The outlining of an overview on the synthesis methods of chelating sorbents with grafted groups is followed by the highlighting of their distinctive properties. In this context, the features of 2 functionalized polymers, namely commercial aminomethylphosphonic resin Purolite S – 940 and chelating ion exchanger with hydroxamic acid and amidoxime groups, that were studied in terms of their potential applicability for the removal of heavy metal ions [Pd(II); Pb(II)] from industrial effluent, have been briefly described. Afterwards, the

results of the studies suggesting that two new proposed chelating sorbents (acrylic copolymers bearing amidoethylenamine and dimethylaminobenzaldehyde functional groups) are very promising candidates for the sorptivepreconcentration and recovery of Pt(IV) and Au(III) from acidic chloride media are systematized.

2.2.1.3. *Ion exchangers modified with chelating reagents*

The main disadvantages of chelating sorbents with grafted functional groups related to the synthesis difficulty and low reversibility of sorption – desorption processes have been prompted the researches for finding of new, simple and fast procedures applicable in their synthesis. A viable alternative is represented by the "sorption" of chelating organic reagents on ion exchangers. Thus, in order to broaden the range of chelating sorbents with improved performance in the recovery of Pd(II), the macroporous anion exchanger Purolite A-500 (in chloride form) has been loaded with 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Ferron). The work has been carried out in batch conditions, in 2 stages (the study of Ferron retention on the anionic resin →the sorption study of Pd(II) on Ferron-loaded resin) and the obtained results emphasized that the macroporous anion exchanger Purolite A-500 loaded with Ferron is eligible as good sorbent for Pd(II) recovery.

The anion exchangers modified with chelating reagents can be used for the selective separation and concentration some microelements, as well as to develop new methods of analysis that combine the concentration of metallic ions in aqueous media with subsequent determination directly in the resin phase. By capitalizing on this opportunity, new methods of Pd(II) and Rh(III) determination by solid-phase spectrophotometry have been proposed.

The proposed methods are based on the retention of platinic metal ions on the Dowex 1x1 anion exchanger loaded with disodium1-nitroso-2-hydroxynaphthalene-3,6 disulphonate (Nitroso – R salt) (20 μmol/g of resin) and the absorbance measurement of the red complexes formed in the resin phase. A comparison with conventional spectrophotometric methods revealed that the proposedmethod is simple, reproductibileand accurate and can be an inexpensive tool for trace analysis. The results obtained on synthetic solutions clearly indicate the feasibility of the proposed method for real sample analysis.

2.2.1.4. *Impregnated sorbents*

A simple and rapid technique of impregnated sorbent preparation is based on "the mechanical impregnation" of the inert matrix with complexing reagents. For this reason, the support is treated with the solution of the complexing reagent in an organic reagent, which is then removed by filtration or evaporation. Thus, by impregnation of 5, 7–dibromo–8 – hydroxyquinoline

(bromoxine) on the polystyrenic non–polar support Purasorba chelating sorbent, particularized by a high selectivity towards Pd(II) ions have been developed.

2.2.2. *Sorbents Based on Polyurethane Foams*

This part describes the performances of some batch and dynamic systems of metal ions separation/preconcentration based on untretated polyurethane foams and modified polyurethane Batch sorption experiments for Pb(II) retention onto.

Section 2.3.

The results of the studies related to the assessment of recovery and treatment possibilities of different indigenous wastes acting as low-cost sorbents of heavy metal ions (Fig. 2) are systematised.

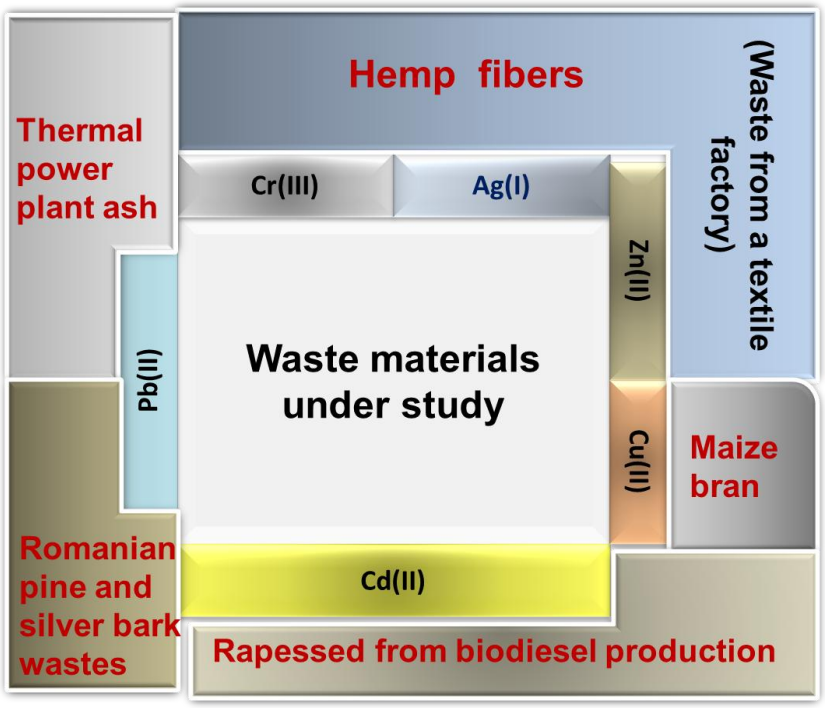

Fig. 2 – Waste materials explored as low – cost sorbents.

The studies on *the feasibility of the conversion of industrial and agricultural waste into value-added sorbents, applicable in advanced treatment of wastewater* have been validated by the 15 papers (11 as first author /

corresponding author) published in ISI journals and the 11 published in BDI journals.

2.3.1. *Hemp Fibers – Waste from a Textile Factory*

The results of batch studies pointed out that the sorption of the Cr(III), Cu(II), Ag(I), Cd(II), Zn(II) and Pb(II) ions on natural hemp fibers is very well described by the Langmuir isotherm model and follows a pseudo–second order kinetics. In order to improve the sorption performances of this material, the hemp fibers have been physically and chemically modified. By using sulphydryl hemp fibers the concentration of Cd(II) in wastewaters might be reduced below allowable discharge limits. The recovered cadmium was greater than 95% and cadmium concentration factors over 30 have been achieved. The results of the performed studies strongly suggest that natural and modified hemp fibers may be promising sorbents provided for environmental technologies in the future.

2.3.2. *Waste of Rapeseed from Biodiesel*

The results systematized in section 2.3.2. give the evidence of the possible benefits of using *the rapeseed waste* from biodiesel production for the removal of heavy metals from aqueous media. The rapeseed, in the batch experiments, was found to be very efficient in removing copper, cadmium or zinc ions from aqueous solutions. The process is strongly affected by several parameters such as: initial pH of the solution, sorbent dose, initial metal ion concentration and contact time. The thermal stability of the rapeseed before and after Zn(II) biosorption was studied by thermogravimetric analysis. It was found that the zinc loaded rapeseed exhibits a better initial thermal stability than the original rapeseed, presumably due to the cross linking generated by the intermolecular complexation of Zn(II) ions. The amount of retained metal determined on the basis of the residue amount remaining at the temperature of 55^{o}C was in good agreement with that obtained by batch sorption studies. Pb(II) sorption capacity for 50 mg/L and 100 mg/L feed concentration of lead ions were higher than the batch conditions for the same initial concentrations, indicating the prefference of the biosorbent to column mode operation. Column studies with real industrial wastewater presented a removal efficiency of 94.47% for Pb(II) and a general improvement of the other quality indicators from the effluent showed the practical utility of the biosorbent.

2.3.3. *Romanian Bark Wastes*

The potential of Romanian pine (*Pinus sylvestris* L) and silver fir (*Abies alba* Mill) bark wastes as green and economical sorbent for Cu(II), Zn(II) and Cd(II) ions removal from aqueous solutions has been tested in batch conditions

as function of initial pH, sorbent dose, metal ion concentration, contact time, and temperature. Equilibrium (Langmuir and Freundlich isotherm), kinetics and thermodynamics of the considered sorption processes were discussed in detail. The utility of Romanian *Abies alba* bark has been demonstrated by removing Cu(II) along with other species from industrial electroplating wastewater. A concentration of Cu(II) as high as 5.25 mg/L in wastewater can be reduced to 0.51 mg/g. The results indicate that sorption can be a viable alternative for bark valorization purposes.

2.3.4. *Thermal Power Plants*

The results in section 2.3.4. are good prospects for the sorption of toxic metals by fly ash in practical applications. It is evident that pH, ash dose, initial Cu(II), Zn(II), Pb(II) and Cd(II) ions concentration, temperature and contact time have marked effect on the sorption. The equilibrium data are best explained by Langmuir sorption isotherm. Thermodynamic parameters also favor the sorption of heavy metal ions under study on energy pit coal ash. Kinetics of sorption follows pseudo – first order rate equation. This valuable use of fly ash will not only convert this waste material into low- cost effective sorbent, but also provide a viable solution to its disposal.

LAVINIA TOFAN
"Gheorghe Asachi" Technical University of Iaşi,
"Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection
e-mail: lavinia_tofan@yahoo.com