BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 63 (67), Numărul 4, 2017
Secţia
CHIMIE şi INGINERIE CHIMICĂ

HABILITATION THESIS SUMMARY

Advanced Capitalization of the Fly Ash to Obtain New Materials

The habilitation thesis presents the original and relevant results in the field of capitalization of fly ash, with application in chemical engineering. In this thesis new synthesized low-cost sorbents, based on Holboca ash, were comparative studied for the removal of heavy metals from aqueous solutions. The synthesis method was very simple under room temperature to high conditions and final product can be safely disposed. The ashes are produced in power plants and represent the largest source of energy. The production of this material (the by-product) is estimated to be more than 370 Mt last years. Ash can be modified and used as sorbent efficient for the removal of heavy metals and dyes from solutions. The modified ash has composition similar to natural zeolites. The ash and modified ash present low cost and efficiently adsorbents, which can be used for removal pollutants from water, gas and soil.

Habilitation thesis “*Advanced capitalization of the fly ash to obtain new materials*” present the scientific work of the author in the last 8 years at the Faculty of Chemical Engineering and Environmental Protection Iaşi, Department of Chemical Engineering.

The thesis includes a part of the results from the synthesis and characterization of new materials: geopolymers and new materials with adsorbent properties used in advanced treatment of water containing heavy metal ions and dyes, ensuring an advanced capitalization of fly ash.

Due to economic progress based on consumption, has become a necessity the replacement of natural resources from industrial processes with

some wastes for getting new products. Under the conditions of reduction and depletion of raw materials, the idea to elaborate some technologies that enabling complete and complex full use as secondary resources, appears more strongly.

Taking into account the concept of sustainable development, the by-product (the waste) of one industry can be a raw material for other industries. The capitalization in order to obtain new products, in addition to the economic side has an important impact on the environment by saving raw materials and reducing pollution caused by storage.

In the last years, it was established research programs that ensure continuous improvement of existing technologies and creation of new technologies, modern and efficient, which ensure a better use of waste.

In the production process of electrical and thermal energy from solid fuels, inevitably a large amount of waste is generated. Worldwide, every year is generated large amounts of industrial waste/ by-products which if it´s not recovered are stored, causing the dismantling of large areas of land. The fly ash resulted from coal combustion in power plants represents the main industrial waste; because of its composition and properties, this waste is among the best secondary raw materials. Currently, along with other energy sources, fuel combustion in power plants occupies an important place in the production of electrical and thermal energy. As a source of energy, the coal is used in power plants, worldwide. The International Energy Agency reported that over 25% of total energy demand is obtained by burning coal, while electricity production is based on coal and peat at a rate of over 40%.

Characterization of fly ash, indicated the main areas of its capitalization. Among these, in the first place is capitalization as additive for new construction materials. The fly ash, along with other types of waste or by-products such as slag, silica fume, volcanic tuff, marble waste, ultrafine clay, demolition waste, agricultural waste etc., is used in the industry of building materials: getting regular or performing concretes, additive in cements composition as the addition or replacement of fine part in polymer concert's, etc. Even if it is used without a prior processing, by addition of ash, new polymeric material with high mechanical properties and high resistance to chemical agents can be obtained.

On the other hand, the change of the ashes by alkali attack may lead to new geopolymeric materials that can successfully replace Portland cement, achieving significant energy savings and significantly reduce carbon dioxide emissions. Also, experimental studies have shown that the modified ash by alkali attack determines the obtaining of materials with adsorbent properties which may be used for the retention of heavy metal ions and coloring agents in the water.

In this context, the **general objective** is to obtain new materials based on ash, allowing a higher capitalization of it, both in building materials and as adsorbent in the processes of removing inorganic and organic pollutants.

Studies were focused on:

- **Capitalization of the unmodified ash**. The ash was used as filler with obtain new materials. For the unchanged ashes, the adsorption capacity for heavy metal ions and coloring agents was studied and the way in which the simultaneous presence of two types of pollutants affect each other.
- **Capitalization of the modified ash by alkali attack.** Alkaline attack was aimed to obtain geopolymeric materials used as a cement replacement and new adsorbent materials.

The specific objectives were:

- ***obtaining and characterization of new types of materials*** with the addition of ash;
- ***establishing by neural network optimum content of ash*** to obtain new materials with required properties;
- ***physico-chemical characterization of the materials*** obtained by alkali attack: scanning electron microscopy SEM, BET specific surface area, the chemical elemental composition, FT-IR spectroscopy, determination of crystallinity by X -ray diffraction and thermogravimetric analysis;
- ***the study of the absorption capacity*** of the ash and of the new materials based on ash for removal of heavy metal ions: copper, cadmium, lead, nickel;
- ***the study of the influence for different parameters:*** pH, s/L ratio, the concentration of the initial solution, time of contact on the removal of heavy metal ions from solutions;
- ***kinetic and thermodynamic modeling*** of adsorption process;
- ***setting the experimental conditions*** for obtaining new materials, based on ash, with the maximum adsorption capacity.

Habilitation thesis is structured into 5 chapters:

Chapter 1 ***The current state of scientific research in the studied field*** - presents a summary of the literature on the ash characterization, the main directions of its capitalization, methods used for change it and the potential applications of ash-based materials..

Chapter 2 presents ***The strategy of experimental research***: in which conditions the modified occurred, the equipment used to characterize new materials, reagents and methods for investigating the ability of new materials to removal various pollutants in aqueous solutions. The ash samples were subjected to direct conversion by treatment with alkali hydroxides in an aqueous solution or as a solid at various temperatures ranging from ambient temperature to 150°C, and different times of contact from 2 hours to 7 days. After a time of contact about 2-4 hours the ash surface changes. The most effective change agent turned out to be 2N NaOH solution. After the attack, the samples undergo crystallization and removal reagent excess by washing.

Chapter 3 shows the results obtained for the ***Characterization of fly ash and new materials***: scanning electron microscopy, determining the BET

specific surface area, elemental chemical composition of macro- and microelements, FTIR, determining the crystallinity by XRD and TG/DTA.

The composition of the studied ashes is relatively uniform, predominantly oxide compounds, differing by the content of unburned carbon. The sum of oxidic components (SiO_2, Al_2O_3 and Fe_2O_3) is over 75%, the ashes can be included in Class F. The soluble compounds (oxides of metals from groups I and II) are not present in large quantities, demonstrated by the total content of soluble salts, conductivity and pH, does not require a washing step prior to capitalization.

Diffraction tests, FT-IR spectral analysis, SEM, BET surface area determination, porosity and surface energy confirms the conversion processes of waste through dissolution-precipitation altering the surface appearance with significant influence on the adsorption capacity. These materials have proven effective in the treatment of wastewater from electroplating, water containing radionuclides and water from the textile industry. After depletion, these adsorbents can be reused as fillers in polymer concrete or to obtain pavers.

Chapter 4 – ***The capitalization of unmodified (raw) fly ash*** presents the experimental results for new polymer concrete with the addition of ash, establishing optimal composition in order to obtain some required properties, along with studies of sustainability. The fly ash in a proportion of 12.8 % and a particle size under 40 μm has a favorable effect on the microstructure of the composite materials. The durability of new materials with fly ash as filler was increase comparatively with other filler.

For cases when the absorption cannot be achieved in wastewater treatment plants or the sorbent could not be regenerated, I analyzed the adsorption capacity of the unmodified fly ash, proving that it has a very good adsorption capacity, especially for Pb^{2+} ions. In the systems containing organic pollutants and heavy metals, competing adsorption can alter the substrate by dye rapid binding, with no effect on the removal of heavy metals.

Chapter 5 – ***Capitalization of the modified ash in adsorption processes*** presents the results obtained for the use of new materials as adsorbents in removal processes of metal captions from solutions. Kinetic studies were carried out by the adsorption of copper ions, cadmium, lead and nickel. It was checked adsorption isotherms using Langmuir and Freundlich models and perform kinetic modeling of the process. The neural network modeling allowed to establish the optimal parameters for the process of alkaline attack. Using the optimized parameters (time of contact, the ash mass/volume of solution), the adsorption process of the cations of: Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} was studied and modeled.

Spectral analysis, XRD and EDX of adsorbents, loaded with pollutants after adsorption, indicates new bonds between pollutants and active sites from the surface of modified ash.

Adsorption reactions arising particularly after a 2^{nd} order pseudo-kinetics and diffusion intra-particles.

The materials obtained by hydrothermal process in an alkaline medium turned out to be effective, the only drawback is the difficult separation of the adsorbent. The results can be applied in the design of an efficient and industrialized process for advanced treatment of wastewater suitable to a wide range of concentrations and types of pollutants.

The last chapter ***General conclusions*** of habilitation thesis are presented in Chapter 6.

The research activity in the field of fly ash recovery led to original results published in 22 papers in ISI journals, 11 papers published BDI, 7 in proceedings of conferences and 22 papers presented at International Conferences. The results were obtained in collaboration with research teams from "Gheorghe Asachi" Technical University of Iaşi; "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine of Iasi, Faculty of Agriculture; "Vasile Alecsandri" University of Bacău, Faculty of Engineering; Department of Chemistry, Aristotle University, Thessaloniki, Greece.

The activity research, materialized in over 155 articles, of which 50 in prestigious ISI quoted journals and 32 in indexed databases journals, with national and international visibility, demonstrated by the 278 citations in Web of Science and Scopus, confirms the ability to lead and guide working groups, including doctoral candidates.

MARIA HARJA

"Gheorghe Asachi" Technical University of Iaşi,
"Cristofor Simionescu" Faculty of Chemical Engineering and
Environmental Protection
e-mail: mharja@ch.tuiasi.ro