Several spherification processes were applied to obtain porous geopolymer spheres, different in term of porosity, specific surface area and adsorption properties. The processes are based on the formulation of metakaolin-based geopolymer slurries, produced using a potassium- or sodium-based alkaline activating solution, and exploiting an injection-solidification method in different mediums, i.e. polyethylene glycol (PEG), liquid nitrogen or calcium chloride, to produce the spheres. When liquid nitrogen was used, the geopolymer slurries underwent a maturation step (several hours at room temperature) to trigger the geopolymerization without reaching a complete chemical consolidation. Spheres were obtained injecting in liquid N$_2$ the mixture as is or mixed with water, to modulate the final porosity (ice-templating process). The spheres were then freeze dried to remove the solidified water and complete the chemical consolidation of the geopolymer.

Conversely, with the PEG solutions, the slurries were directly injected in the solutions heated at different temperature (60-80°C). After the consolidation, the spheres were rinsed with water and left in a heater to complete the geopolymerization.

Geopolymer slurries were also mixed with a solution of sodium alginate and then dropped off in a hot CaCl$_2$ solution to obtain spheres by means of an ionotropic gelation.

The object of the work was to synthetize geopolymer spheres with hierarchical porous structures differing in term of intrinsic mesoporosity and architecture, which means distribution of voids/material within the spheres (Fig. 1). The production process parameters were deeply investigated together with the different geopolymer slurry compositions in order to design the final porous structures of the spheres; indeed the tuning of the water content in the starting mixtures allows to affect the intrinsic mesoporosity of the geopolymer matrix (water is a pore former during the geopolymerization), moreover, the porosity can be further tailored adding organic templates as the alginate.

The design of the porosity in the final spheres is important to find potential applications, indeed, beads and spheres have received attention for their potential use as adsorbents, microreactors, catalysis supports, etc., thanks to the good mobility, flow-ability, high packing density, ease of separation and reuse after regeneration. Hence, the most performing spheres were selected and characterized in term of morphology, macro- and microstructure, composition-stoichiometry, porosity distribution and specific surface area together with the adsorption properties towards, for example, gaseous CO$_2$ or dyes and heavy metals in aqueous solution.