

Abstract

This Ph.D. thesis was developed within the framework of the NANOSUSTECH project, part of the MICS Extended Partnership, funded under the PNRR – Mission 4, Component 2, Investment 1.3 – D.D. 1551 of 11/10/2022, project code PE00000004. The research focused on the antibacterial functionalization of nanostructured materials for air and water purification applications, aiming to design and investigate sustainable and effective strategies for incorporating inorganic metal-based antimicrobial agents into different filtration-related substrates, including electrospun polymeric fibers and natural zeolites.

Three main functionalization approaches were explored: i) the deposition of antimicrobial coatings, ii) the *in situ* synthesis of antibacterial nanoparticles directly on substrate surfaces, iii) the incorporation of active phases during electrospinning. Low-temperature coating techniques, such as co-sputtering and plasma-enhanced chemical vapour deposition, were applied to thermally sensitive electrospun fibers in order to preserve their morphology while introducing antibacterial functionality. Ag-containing oxide nanocomposite coatings based on SiO₂ and ZrO₂ demonstrated the potential of dry deposition methods for producing effective antimicrobial fibrous filters. In parallel, PECVD-based coatings highlighted the importance of the spatial distribution and interaction between different active phases, particularly silver and zinc oxide, in enhancing antibacterial performance.

In addition, polysilazane-derived coatings were explored as ceramic-like composite systems obtained from preceramic polymers. The compatibility between Durazane 1800 and Ag-decorated silica nanospheres was demonstrated, although no significant antibacterial activity was achieved. Nevertheless, the processing advantages of polysilazanes opened a broader research direction beyond the main antibacterial focus of this thesis, particularly toward additive manufacturing of ceramic components, whose preliminary results are presented in Appendix A.

Green synthesis routes based on natural polyphenolic compounds were also investigated for the *in situ* synthesis of metal-based nanoparticles. Tannic acid was successfully used to functionalize natural clinoptilolite and porous polymeric fibers with Ag-based nanoparticles, showing that the amount, oxidation state, and release behaviour of silver can be modulated through processing conditions such as pH. Copper-based systems were also explored, although their higher chemical complexity requires further optimization. Curcumin was additionally considered as a promising hydrophobic polyphenolic agent for the synthesis and stabilization of Ag nanoparticles in polymer-compatible environments.

Finally, the direct incorporation of antibacterial nanoparticles during electrospinning was studied. Ag nanoparticles synthesized in the presence of PVP were introduced into PAN fibers, leading to hybrid fibrous materials with antibacterial activity and tunable release behaviour. Additional preliminary work on porous PLA fibers suggested the potential of integrating green nanoparticle synthesis with wet electrospinning processes.

Overall, the thesis demonstrates that nanostructured materials can be effectively functionalized with metal-based antimicrobial agents through tailored processing strategies. The antibacterial response can be controlled not only by the type and amount of active phase, but also by its chemical state, spatial distribution, interaction with the substrate, and stabilization mechanism. These findings provide a basis for the development of advanced antimicrobial materials for filtration applications, while future work should focus on long-term stability, durability under realistic operating conditions, release behaviour, and the environmental implications associated with nanoparticle-based systems.

