Hydrogel-based systems for controlled release of antidotes and decontaminants

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Abstract

This doctoral thesis addresses the development and evaluation of advanced analytical methods and functional materials for the identification, decontamination, and mitigation of chemical warfare agent (CWA) exposure. The research integrates four complementary experimental approaches, combining analytical chemistry, nanostructured materials, and polymer-based systems to improve chemical defense capabilities.

The first research direction focused on developing and optimizing complementary GC–MS/MS and LC–MS/MS methods for the identification of specific biomarkers of exposure to nerve and blister agents in biological matrices. The investigation included hydrolysis products, intact compounds, and protein adducts, with particular emphasis on the analytical characterization of A-series nerve agents. The developed methods demonstrated high selectivity and applicability to complex biological samples, with their performance further supported by OPCW interlaboratory proficiency testing.

The second direction involved developing reactive organic decontamination suspensions incorporating ZnO, TiO_2, and zeolite. Experimental evaluation against sulfur mustard (HD) and soman (GD) demonstrated rapid decontamination, with selected formulations achieving approximately 95% HD removal within 2 minutes and over 99.9% GD decontamination. Furthermore, the identification of degradation products provided additional information regarding the chemical transformation pathways.

A further innovative contribution consisted of developing peelable, calcium-crosslinked hydrogels based on alginate, hydroxyethyl cellulose, and gum arabic, functionalized with metal–organic frameworks. The optimized formulations containing ZIF-8 achieved decontamination efficiencies exceeding 80% within 10 minutes, combining rapid contaminant removal with partial chemical transformation and improved mechanical properties.

Finally, photocrosslinked hydrogels incorporating halloysite, TiO_2, and cyclodextrines were investigated as controlled-release systems for atropine sulfate. The β-cyclodextrin-based formulation exhibited the most promising sustained-release behavior, highlighting its potential for further development in antidote delivery applications.

The principal novelty of this thesis lies in the complementary integration of advanced biomarker identification strategies, reactive nanostructured decontamination systems, multifunctional peelable hydrogels, and controlled antidote delivery platforms. Collectively, these contributions provide an experimental foundation for developing integrated approaches to chemical warfare agent exposure management, with potential applications in CBRN defense and biomedical protection.

The PhD thesis outlines 222 pages