



MULTISCALE THEORETICAL INVESTIGATION OF HEAVY METAL AND ORGANIC POLLUTANT SORPTION ON FUNCTIONALIZED CELLULOSE DERIVATIVES

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Relevance: Water contamination by heavy metals (Pb^{2+} , Cd^{2+} , Ni^{2+}), metalloid ions (As(III) , As(V) , Cr(VI)), and persistent organic pollutants (phenolic derivatives, pharmaceutical residues, dyes) remains a major environmental concern worldwide. Conventional water treatment methods are often insufficient to achieve both high efficiency and selectivity. In this context, biopolymeric sorbents based on modified cellulose offer significant advantages due to their biocompatibility, availability, and ease of functionalization. Dialdehyde cellulose grafted with thiosemicarbazide (DAC@TCH) and its thiol-functionalized derivative (DAC@TCH-SH) are particularly promising candidates for the selective binding of toxic metal ions and organic pollutants.

Objective: The present study aims to provide a comprehensive theoretical investigation of the sorption properties of DAC@TCH and DAC@TCH-SH toward heavy metals, oxyanions of arsenic and chromium, and representative organic pollutants using density functional theory (DFT), quantum theory of atoms in molecules (QTAIM), molecular orbital analysis, and molecular docking.

Materials and Methods: All structures were optimized, and binding energies were calculated at the $\omega\text{B97X-D/def2-TZVP}$ level with the SMD solvation model for water. Counterpoise corrections were applied to account for basis set superposition error (BSSE), and thermodynamic corrections (ΔG_{298}) were included. Donor–acceptor interactions were examined by Natural Bond Orbital (NBO) analysis. The spatial distribution of the electron density and bond critical points were analyzed via QTAIM. Electronic properties, including HOMO–LUMO gaps and projected density of states (PDOS), were employed to discuss the nature of the interactions. Molecular docking was performed to evaluate the antimicrobial potential of the sorbent–pollutant complexes against bacterial proteins of *Escherichia coli* and *Staphylococcus aureus*.

Results: DFT calculations revealed that Pb^{2+} and Cd^{2+} exhibit the strongest interactions with DAC@TCH-SH , with significantly enhanced binding due to S-donor coordination. Nitrogen and oxygen donors provided weaker stabilization, consistent with HSAB principles. For oxyanions As(V) and Cr(VI) , sorption was dominated by hydrogen-bonding networks involving NH and OH groups, with little effect of thiol modification. Organic pollutants displayed variable behavior: tetracycline and methylene blue showed strong binding through a combination of hydrogen bonding, π – π stacking, and electrostatics, while bisphenol A and 4-nitrophenol bound moderately. QTAIM confirmed partial covalency in Pb–S bonds ($\rho(r) \approx 0.08$ a.u.) and closed-shell characteristics of hydrogen-bond interactions with oxyanions. Molecular docking suggested that sorbent–pollutant complexes could interact with bacterial proteins, highlighting a potential antimicrobial synergy.

Conclusions: This study demonstrates that thiol functionalization markedly enhances the sorption performance of cellulose-based adsorbents toward soft heavy metals (Pb^{2+} , Cd^{2+}), while maintaining high activity against oxyanions and organic pollutants. DAC@TCH-SH exhibits dual



functionality, serving both as an effective sorbent and as a potential antimicrobial agent. The obtained results provide theoretical guidance for the rational design of multifunctional biopolymer-based materials for water purification and environmental protection.