

Quantum calculation on the reductive degradation of carbon tetrachloride by vivianite

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Reductive degradation of chlorinated organics by natural soil minerals has been extensively studied for sustainable remediation of contaminated soil and groundwater. In this study, we investigated the reductive dechlorination of carbon tetrachloride (CT) by vivianite ($\text{FeII}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$) in batch system. A variety of environmental factors such as concentration of CT, suspension pH (pH 5 ~ 9), and presence of major competing ions (Ca^{2+} , HCO_3^-) significantly affecting the degradation rate of CT. Concentration profiles of transformation products were monitored to discuss the degradation pathway of CT by vivianite. Quantum calculation (QC, Density Functional Theory method, software: Maestro and Cerius 2) was used to estimate binding energy among relevant chemical species in the system to explain molecular scale interaction on the vivianite surface. The results have shown favorable intermediates and detailed decomposition mechanism throughout the dechlorination pathway of CT. HCCl_3 does not seem to be dechlorinated directly on the surface of vivianite, due to positive binding energy from 1.637 eV to 5.178 eV. Instead, Cl- atoms could be exchanged by OH- and water, leading to the formation of HCOOH as main transformation product. The experimental and theoretical results obtained from this study can be properly applied to the design and operation of enhanced natural attenuation for the reductive dechlorination of CT.