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### Effect of natural organic matter on the reductive dechlorination of chlorinated hydrocarbons by surface-mediated Fe(II) associated with goethite

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Fe(II) is one of the most abundant reductants available in subsurface condition. Fe(II) ions are able to reduce priority pollutants if they are associated with iron mineral surfaces or available as structural Fe(II). Reductive dechlorination of chlorinated hydrocarbons by Fe(II) associated with iron minerals has been studied before several years for possible use of such systems for natural attenuation of ground water in contaminated sites. The pH of the system, concentration of surface-bound Fe(II) ions and surface area of iron oxide have been identified as major controlling factors for the dechlorination reaction rates. However, there is no detailed reports documented the effect of humic substances on the reactivity of Fe(II)-iron mineral systems although they are ubiquitous in natural environment. Present study was carried out to study the effect of humic acid (HA) on the reactivity of Fe(II) associated with goethite ( $\alpha$ -FeOOH) system for the dechlorination of CCl<sub>4</sub>. Since quinone compounds contain functional groups those are supposed to be active in redox reactions, Anthraquinone 2,6-disulphonic acid (AQDS) (C<sub>14</sub>H<sub>6</sub>O<sub>8</sub>S<sub>2</sub>Na<sub>2</sub>) and Lawson (2-hydroxy-1,4-naphthoquinone (C<sub>10</sub>H<sub>6</sub>O<sub>3</sub>) were also used representing quinone compounds (QC) instead of HA. Reactors used were 50-ml amber bottles sealed with black viton caps and aluminum crimps. All the preparations were done in an anaerobic glovebox. Parallel replicates of experiments were carried out using Goethite ( $\alpha$  FeOOH) alone, and equilibrated heterogeneous system of goethite - aqueous Fe(II) in the absence and presence of reduced form of both HA and QC separately for dechlorination of CCl<sub>4</sub> (0.65  $\mu$ M) at 7.1  $\pm$  0.1. The major target compound CCl<sub>4</sub> and its product were identified and quantified by GC-MS head space method. Results show that HA and QC could degrade CCl<sub>4</sub> following 1<sup>st</sup> order reaction kinetics with the observable rate constant ( $k_{obs}$ ) of 0.024d<sup>-1</sup>, 0.014d<sup>-1</sup>, 0.028d<sup>-1</sup> and 0.029d<sup>-1</sup> for AQDS, LQ, reduced HA and native HA amended systems respectively. Under the same conditions but in the presence of Fe(II) (0.1mM) the  $k_{obs}$  values were 0.035d<sup>-1</sup>, 0.051d<sup>-1</sup>, 0.041d<sup>-1</sup> and 0.04d<sup>-1</sup> respectively showing that Fe(II) ions can increase the rate constant by 1.45, 3.64, 2.92 and 1.42 times making the system more reductive. Dissolved Fe(II) alone could not dechlorinate CCl<sub>4</sub>. Dechlorination of CCl<sub>4</sub> occurred with  $k_{obs}$  of 0.087d<sup>-1</sup>, 0.3d<sup>-1</sup>, 0.46d<sup>-1</sup>, 0.38d<sup>-1</sup> and 0.37d<sup>-1</sup> in the systems of Goethite-Fe(II) alone, and with AQDS, Lawson HA(reduced) and HA (native) respectively. This study clearly shows that HA and QC can significantly increase the reactivity of iron mineral -Fe(II) system for degradation of CCl<sub>4</sub>.