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Transformation of iminodi(methylene phosphonate) on manganese dioxides – passivation of the mineral surface by formed Mn^{II}

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Aminopolyphosphonates (APPs) are strong complexing agents for divalent cations and used as bleaching stabilizers, detergent additives, and anti-scaling agents. Due to increasing use in household and industrial applications and incomplete removal during wastewater treatment, APPs were detected in surface waters in the µg L^{-1} range. [1]

Knowledge about their environmental fate and possible adverse environmental effects is scarce. Yet it is known that aminomethyl phosphonate (AMPA) is a major transformation product of A(P)Ps. [2,3]

A possibly important transformation mechanism in the environment is the oxidation on manganese oxides (MnO_x), which belong to the strongest naturally occurring oxidants and are commonly present in soils and sediments. [4] Transformation of aminotris(methylene phosphonate) (ATMP) to iminodi(methylene phosphonate) (IDMP) on MnOOH has already been shown. [5]

In this work, we investigated the transformation of IDMP on MnO_2. IDMP served as a model compound, as it presents a transformation product (TP) of many higher APPs and is a precursor of AMPA. [5] To shed light on the processes at the mineral surface, quantitative analysis of aqueous and sorbed fractions of IDMP and its TPs AMPA, phosphate and Mn^{2+} was coupled with kinetic modelling and compound-specific stable carbon isotope analysis (carbon CSIA) of the remaining fraction of IDMP.

AMPA and phosphate were proven to be the main TPs of IDMP oxidation by MnO_2. Further, our results indicate passivation of the MnO_2 surface by sorption of Mn^{2+} formed during the reaction. Based on these observations, we propose the formation of a ternary surface complex between MnO_2, Mn^{2+} and IDMP to rationalize that high Mn^{2+} concentrations on the surface cause i) higher sorption of IDMP but also ii) slower reaction kinetics by inhibiting electron transfer between IDMP and MnO_2.

References

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