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Adsorption and transformation of the anthelmintic drug niclosamide by manganese oxide

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Abstract

The manganese oxide birnessite adsorbed and catalyzed the transformation of the anthelmintic drug niclosamide (NIS) into 2-chloro-4-nitroaniline (CNA) and 5-chlorosalicylic acid (CSA) at acidic pH. The adsorption of NIS was fitted using a linear isotherm for all conditions and reaction times. Linear adsorption constant K_d was 103 000 L kg^{-1} at pH 5.0. The rate of transformation was first order with respect to both MnO_2 and NIS. At pH 5.0, the second order rate constant was $3.3 (\pm 0.3) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$. The adsorption constants and the rates of transformation decreased when pH increased from 4.0 to 5.5 because of increasing electrostatic repulsions between both negatively charged manganese oxide surface ($\text{pH}_{\text{zpc}} = 2.5$) and NIS ($\text{pK}_a = 6.38$). The presence of natural organic matter (NOM) extracted from surface water also significantly decreased the adsorption and the rates of transformation of NIS. The rate of transformation decreased by a factor of 20 in presence of 1.6 mgC L^{-1} even though significant amounts of NIS were adsorbed onto MnO_2 . The interactions between NOM and NIS were investigated by using the fluorescence quenching method and would explain that NIS adsorbed on the surface of manganese oxide was stable in presence of NOM. Thus, hydrolysis catalyzed by manganese oxide is probably not an important process compared to biodegradation and adsorption because of the presence of organic matter and pH values usually > 5.5 in aquatic environment.

Keywords: niclosamide, manganese oxide, natural organic matter, adsorption, oxidation.

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