



Oxidation process of dissolvable sulfide by synthesized todorokite in aqueous systems



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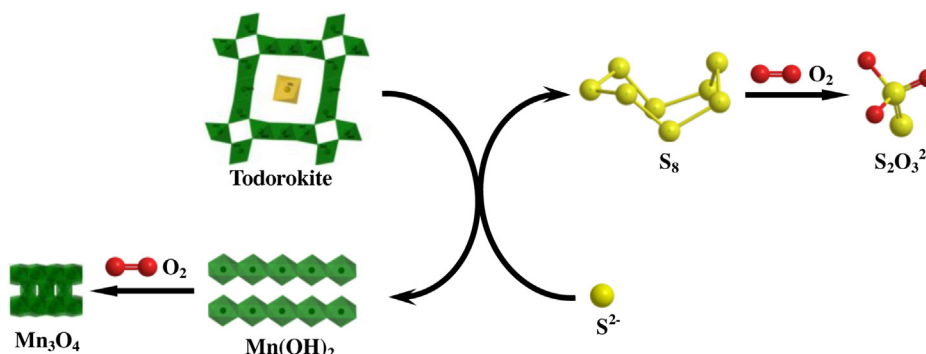
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HIGHLIGHTS

- Elemental sulfur was the main product of sulfide oxidation by todorokite.
- Sulfur was further oxidized to $S_2O_3^{2-}$ by oxygen in open systems.
- The initial oxidation rate of sulfide followed a quasi-first-order kinetic law.
- The initial oxidation rate of sulfide was affected by Mn(III) content in todorokite.

GRAPHICAL ABSTRACT

Elemental sulfur was the main product of sulfide oxidation by todorokite, and was further oxidized to $S_2O_3^{2-}$ by oxygen in open system. During the redox process of sulfide and todorokite, the initial oxidation rate of sulfide followed a pseudo-first-order kinetic law, and was significantly affected by Mn(III) content in todorokite.



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ABSTRACT

Todorokite, formed from Mn(II) in supergene environments, can affect the transformation and migration of dissolvable sulfides in soils and water. In this work, todorokite was synthesized with different degrees of crystallinity, and the redox mechanism of dissolvable sulfide and todorokite was studied in both closed and open aqueous systems. The influences of pH, temperature, crystallinity, the amount of manganese oxides, and oxygen gas on S^{2-} oxidation process were investigated. It is found that S^{2-} was oxidized to S^0 , SO_3^{2-} , $S_2O_3^{2-}$ and SO_4^{2-} , and about 90% of S^{2-} was converted into S^0 in closed systems. The participation of oxygen facilitated the further oxidation of S^0 to $S_2O_3^{2-}$. S^0 and $S_2O_3^{2-}$ were formed with the conversion rates of S^{2-} about 45.3% and 38.4% after 1 h of reaction, respectively, and the conversion rate for $S_2O_3^{2-}$ increased as reaction prolonged for a longer period. In addition, todorokite was reduced to Mn(OH)₂ in the presence of nitrogen gas, and its chemical stability increased when oxygen gas was admitted into the reaction system during the process. The oxidation rate of dissolvable sulfide followed a pseudo-first-order kinetic law in the initial stage (within 10 min), and the initial oxidation rate constant of

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S^{2-} increased with elevating temperature, increasing the quantity and decreasing crystallinity of todorokite. The initial oxidation rate of dissolvable sulfide decreased with continuous feeding of O_2 into the test solution, possibly due to a decrease in active Mn(III) content in todorokite. The present work demonstrates the redox behaviors and kinetics of dissolvable sulfide and todorokite in aquatic environments.

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1. Introduction

Dissolvable sulfide, S^{2-} , is widely distributed in nature, such as sewage, sediment pore water, and acid mine wastewater, due to the industrial wastewater discharge, the decomposition of organic matter, and acid mine drainage [1–4]. High concentration aqueous sulfides are usually generated from the dissociation of polysulfide, FeS_{aq} , and organic compounds [1,3]. As one type of malodorous pollutants, dissolvable sulfides are harmful to the health of humans and animals, and could also cause severe corrosion of metals and concretes [5]. The oxidation of dissolvable sulfides not only leads to soil acidification, but also releases nutritive elements and toxic metal ions, such as Zn, Cu, Pb, Cr and Cd cations [6,7], and promote the reduction of dissolved organic matter [8]. The species distribution, oxidation, and migration of dissolvable sulfides in soils and water, therefore, have gained growing attention recently in environmental chemistry and soil science.

Manganese oxides, present in soils and sediments, exhibit high capabilities for the oxidation and adsorption of valence-changeable metal ions, sulfides and organic pollutants, due to their various crystal structures, mixed valences, large surface areas, and low points of zero charge [1,9–12]. Although the redox behaviors between dissolvable sulfides, particularly S^{2-} , and manganese oxides in soils and marine sediments have been extensively investigated in recent years, most studies only focused on birnessite, vernadite, akhtenskite, pyrolusite, and cryptomelane [9,13–15]. As reported, manganese oxides could be formed with various crystal structures in supergene environments [16]. At near-surface conditions, todorokite, usually generated from birnessite [17], which could be formed by biological Mn(II) oxidation in soils and sediments under ambient conditions in nature [18,19]. Therefore, the todorokite may participate in the oxidation process of dissolvable sulfides. Hence, the interaction mechanism of todorokite and dissolvable sulfides in soils and sediments needs to be further addressed.

Chemical weathering usually occurs in sulfide-bearing mining soils, involving the alteration of iron sulfides, the formation of secondary minerals, and the release of dissolvable sulfide and toxic metal ions [4,20–22]. In these zones, manganese oxides could also be found likely due to the dissolution, hydrolysis and further oxidation of Mn^{2+} leached from tailings [4,21]. Manganese oxides including todorokite are ubiquitous in soils, sediments, and freshwater and marine aquatic environments, which play an important role in controlling the geochemical distribution, migration, and transformation of trace elements and heavy metals, such as As, Cr, Mo and V [21,23–25]. The decrease of pH and Eh will result in the reduction of manganese oxides, and consequently the adsorbed trace elements and heavy metals will be released and dissolved back into aquatic environment [25,26]. The presence of dissolvable sulfide will accelerate the reduction and dissolving of manganese oxides. Therefore, the redox of dissolvable sulfide and todorokite would affect the transformation, migration, and distribution of adsorbed toxic metal ions, and their influence factors for reaction rate particularly deserve further investigation.

Previous researches mainly focused on the single system [8,13–15], however, the combined effect of manganese oxide and oxygen on the transformation process of dissolvable sulfide usually occurs in the open system. To elucidate the reaction pathway

and kinetics of dissolvable sulfide oxidation, methods such as characterization of intermediate products and quantification of the formation rates are employed [8,13–15]. In open environments, oxygen participated in the oxidation process of dissolvable sulfide [1,27]; while in closed systems, sulfur was the main product [14,15], and was further oxidized when oxygen was continuously admitted into the reaction solution [28]. Sulfur, thiosulfate, sulfite, and sulfate were previously identified as the main products in different literatures, which is likely due to the difference in crystal structures of manganese oxides, and reaction conditions including pH, temperature, and oxygen, etc. [13–15]. Therefore, the combined effect of manganese oxide and oxygen on the transformation process of dissolvable sulfide should be studied to illustrate the detailed interaction mechanism in open systems.

Studies suggest that when dissolvable sulfides were oxidized by manganese oxides, active Mn(III) centers are important surface features involved in much of the redox chemistry of manganese oxides [9,10]. It is also found that the initial oxidation rates of S^{2-} are highly dependent on the content of active Mn(III), which is available in manganese oxides [9,15]. The newly generated Mn(III) centers from the reduction of Mn(IV) by S^{2-} may keep the oxidation activity of birnessite [9]. However, Mn(II/III) in manganese oxides could be easily oxidized to Mn(IV) by oxygen in aqueous solution [29]. As for open systems, both oxygen and manganese oxides are involved in the oxidation process of dissolvable sulfide. The changes of manganese oxide crystal structures and chemical composition, particularly Mn(III) content, and the reaction mechanism and kinetics of dissolvable sulfide oxidation need to be further studied.

Fully understanding of the redox mechanism and kinetics of dissolvable sulfide (S^{2-}) and manganese oxides, such as todorokite, would help to control the chemical species, pH, redox potential (Eh), and soil acidification process. To achieve these goals, the oxidation behaviors and kinetics of S^{2-} by todorokite with different degrees of crystallinity were studied in this work. The influences from the amount and crystallinity of todorokite, temperature, and oxygen atmosphere on the oxidation mechanism and transformation rate of S^{2-} were investigated, in particular, for the change of Mn(III) content and the corresponding oxidation rate of S^{2-} in the presence of oxygen. The concentration of S^{2-} and its oxidation products in the solution were characterized by spectrophotography and ion chromatography, respectively. The main products of solid sulfur were quantified by high-performance liquid chromatography, and the change of Mn(III) content in todorokite was characterized by X-ray photoelectron spectroscopy (XPS) when oxygen was pumped into the reaction solution during the oxidation process.

2. Materials and methods

2.1. Chemicals

NaOH, $MnCl_2 \cdot 4H_2O$, CH_3COOH , $Na_2S \cdot 9H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, *N,N*-dimethylphenylenediamine, $NaCH_3COO \cdot 3H_2O$, KI, I_2 , $Na_2S_2O_3$, $K_2Cr_2O_7$, $AgNO_3$, $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$, CH_3OH , and soluble starch were all of reagent grade and purchased from China National Medicine Group Shanghai Chemical Reagent Company. Distilled

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