### **News Release**

### Title

Potential application of a hydrotalcite-like compound for reduction of toxicity to aquatic organisms via rapid and efficient removal of hydrogen sulfide

# **Key Points**

- •MF-HT is a low-cost and safe material for high-efficient removal of H<sub>2</sub>S in water
- •MF-HT reduced toxicities for water microorganisms in groundwater with H<sub>2</sub>S
- •MF-HT has excellent reusability for H<sub>2</sub>S removal in water.

## Summary

Hydrogen sulfide (H₂S) is a toxic gas with a rotten egg odor and is known to occur naturally and artificially in volcanic zones, hot springs, wastewater treatment plants, landfills, and oil refineries, etc. H<sub>2</sub>S is usually generated by sulfate-reducing bacteria that exist in anaerobic condition, such as in the lake sediments. It can be easily dissolved in water and exists as HS-, which is toxic to aquatic organisms at very low concentrations (0.003-2 mg/L). In this study, Professor Masashi Kato's research group investigated the H<sub>2</sub>S removal ability of a patented hydrotalcite-type compound (MF-HT) consisting of magnesium and iron and evaluated its potential application for reducing toxicity to aquatic organisms. The results showed that the MF-HT has a high adsorption capacity of 146.5 mg/g with a fast adsorption equilibrium time of 45 min for H<sub>2</sub>S removal, both of which are top-class compared with those of other adsorbents previously reported. In fact, removal of hydrogen sulfide (1.2-152.5 mg/L) at an average rate of > 97.6% was achieved in groundwater samples (n=16) by the MF-HT within 60 min. The toxicities of groundwater, indicated by inhibition rate for microalgae (primary producers) and immobilization rate for crustaceans (secondary consumers), were reduced by 96.1% and 82.5% in 2-fold and 4-fold diluted groundwater, respectively, after treatment with the MF-HT for 60 min. These results indicate that MF-HT has an excellent safety record for aquatic organisms. After clarifying the adsorption mechanism, excellent reusability of MF-HT was also confirmed after regeneration using 1 M Na<sub>2</sub>CO<sub>3</sub> solution. Considering the efficacy, speed, safety and cost of MF-HT, it could be a novel promising material for solving the problem of hydrogen sulfide pollution in the hydrosphere.

#### Research Background

Hydrogen sulfide ( $H_2S$ ), a highly toxic chemical, can cause damage to multiple organs including respiratory and neural systems. Toxicities of hydrogen sulfide have been shown not only as a gas in the atmosphere but also as dissolved forms (90% as  $HS^-$  at pH > 8.0) in the hydrosphere due to its solubility of 4000 mg/L ( $20^{\circ}C$ ) in water. It has been shown that hydrogen sulfide affects the growth and survival of aquatic organisms such as fish, invertebrates, plants and algae at concentrations as

low as 0.003-2.0 mg/L. Since hydrogen sulfide can be naturally generated by reduction of sulfate or degradation of organic matter in the absence of oxygen by sulfate-reducing microorganisms, it is often detected in groundwater and sediments in water systems. Hydrogen sulfide is also generated anthropogenically from various industrial activities, such as in petrochemical industry, paper and pulp mills, and tanneries and in sewer treatment plants. Therefore, it is important to develop an efficient removal method for hydrogen sulfide in the hydrosphere to maintain the diversity of aquatic organisms and to reduce the dissipation of hydrogen sulfide to the atmosphere in order to prevent health risks for humans and animals living on land. Thus, in this study, we have first investigated the removal capacity of our original adsorbent (MF-HT) for hydrogen sulfide removal in water.

## Research Results

Firstly, the removal capacity of hydrogen sulfide by MF-HT along with contact time was investigated. Equilibrium removal was achieved after 45 min. The kinetics of hydrogen sulfide removal by MF-HT were analyzed using pseudo-first-order and pseudo-second-order models. The kinetic data fitted well to both pseudo-first-order and pseudo-second-order models, indicating the possible mechanisms of physical and chemical interaction on MF-HT. Then, the removal capacity of MF-HT was investigated by varying the initial concentrations of sulfide in water. The adsorption experimental data was analyzed using Langmuir isotherm model. The maximum adsorption capacity estimated from the Langmuir isotherm model was 146.49 mg/g in theory.

The hydrogen sulfide removal capacity of MF-HT in a real application was further investigated using groundwater samples (n=16) obtained in Japan. Hydrogen sulfide in all of the water samples was efficiently removed by MF-HT. The mean concentration of hydrogen sulfide in the water samples was reduced from 23.9 to 0.56 mg/L after treatment with MF-HT, indicating > 97.6% removal of hydrogen sulfide by MF-HT (Fig. 1).

To evaluate the effect of alleviated toxicity for aquatic organisms by MF-HT-mediated removal of hydrogen sulfide, microalgal and daphnia toxicity tests were performed. The rate of inhibition on microalgal reproduction was reduced by 96.1% in 2-fold diluted groundwater after treatment with MF-HT. The immobilization rate of daphnia neonates was reduced by 82.5% in 4-fold diluted groundwater after remediation by MF-HT (Fig. 2).

To clarify the adsorption mechanism using MF-HT,

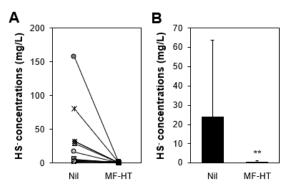


Fig. 1 Removal of hydrogen sulfide from spring water samples using MF-HT.

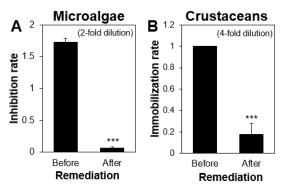


Fig. 2 Toxicity evaluation of spring water samples before and after MF-HT remediation.

analyses by XRD, FTIR and SEM-EDX were performed and changes in the structure and functional groups of MF-HT after hydrogen sulfide adsorption were determined. The results showed that the hydrotalcite-like structure of MF-HT was not affected by the adsorption process, while peaks of sulfate appeared in FT-IR spectra of MF-HT after adsorption and sulfur content was increased on MF-HT after adsorption. These findings indicated that ion exchange of hydrogen sulfide ion and bicarbonate ion may have occurred and that intercalated hydrogen sulfide ion was further oxidized to form sulfate. The results imply that regeneration of MF-HT is possible by using Na<sub>2</sub>CO<sub>3</sub> solution to desorb sulfate from MF-HT. After desorption using 1 M Na<sub>2</sub>CO<sub>3</sub> solution for 30 min, the adsorption capacity of regenerated MF-HT was evaluated. The results showed that the adsorption capacity of regenerated MF-HT (71.32 mg/g) was similar to that of raw MF-HT (72.73 mg/g), indicating excellent reusability of MF-HT for removal of hydrogen sulfide in water.

# Research Summary and Future Perspective

Hydrogen sulfide can be generated in eutrophic sediments of lakes and oceans, which would severely threaten the health and survival of aquatic organisms, especially benthic organisms. Furthermore, hydrogen sulfide in water is continuing to be produced by various industries worldwide. In this study, we found that there was a high level of naturally produced hydrogen sulfide in groundwater. We showed that our adsorbent MF-HT could efficiently remove hydrogen sulfide in groundwater samples and significantly improved the survival ratios of an aquatic animal (crustacean) as well as an aquatic phytoplankton (microalgae). Our results suggest that our MF-HT may be useful for maintaining the diversity of aquatic organisms as well as remediating water pollution caused by naturally and anthropogenically produced hydrogen sulfide. Due to the low cost of MF-HT in addition to its high performance and safety shown in this study, it could be a novel candidate for remediation of water pollution caused by hydrogen sulfide.

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