Removal of hydrogen sulfide with granulated coal ash under aerobic and anaerobic conditions

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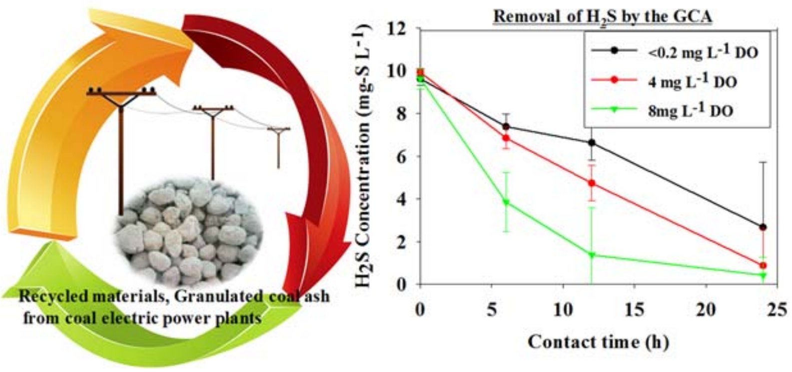
Graphical Abstract



Highlight

GCA is produced through coal fly ash from coal thermal electric power stations.

The removal rate of hydrogen sulfide was investigated by the GCA.

The GCA could remove hydrogen sulfide under both anaerobic and aerobic conditions.

Hydrogen sulfide was removed due to the multiplier effect under aerobic conditions.

Removal of hydrogen sulfide with granulated coal ash under aerobic and anaerobic conditions

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Abstract

Annual emissions of fly ash from the burning of coal have increased to approximately 750 million tons. It is hoped that new applications utilizing by-products from coal-fired power plants will contribute to further waste reduction and set the standard for industrial-scale recycling. The purpose of this study was to evaluate the removal rate of hydrogen sulfide by a new recycled material called granulated coal ash, which is produced from coal fly ash from coal thermal electric power stations and blast furnace cement. A batch experiment was carried out to evaluate the removal rate of hydrogen sulfide by granulated coal ash under both anaerobic and aerobic conditions. The granulated coal ash could remove hydrogen sulfide under both anaerobic and aerobic conditions. However, the maximum removal of hydrogen sulfide by granulated coal ash was only 5.1 mg-S g^{-1} under anaerobic conditions because the manganese oxide which oxidizes hydrogen sulfide to sulfur could not be regenerated under anaerobic conditions. In contrast, the rate constant for hydrogen sulfide under aerobic conditions was high due to the multiplier effect attributed to both increasing Eh and the regeneration of manganese oxide by dissolved oxygen.

Key Words

Blast furnace cement, Coastal Sea, Coal-fired power plant, Eutrophication, Sediment, Recycled material

1. Introduction

Annual industrial emission of fly ash by coal burning is approximately 750 million tons (1). In 2011, coal-fired generation accounted for 29.9% of the world's electricity supply, and it is estimated that this will increase to 46% by 2030 (1). Coal ash has been recycled for various uses—as a key ingredient in concrete and road base construction, as a soil amendment, for zeolite synthesis, as a raw material for extracting rare earth elements, and as an absorbent (1-5)—and its utilization percentage is approximately 50–70% (1). Therefore, the present utilization rate is insufficient for complete recycling of the increasing amounts of coal ash being produced. It is hoped that new and expanded applications for coal fly ash will contribute to further waste reduction and set the standard for other industrial-scale recycling.

In the past few years we have developed a recycled material for environmental remediation of coastal oceans called granulated coal ash, GCA (6). GCA is produced through the granulation of coal fly ash from coal thermal electric power stations (Chugoku Electric Power) with added blast furnace cement as binder amounting to 13–15% of the final product. When coal fly ash is mixed with blast furnace cement, the Pozzolanic reaction (7) occurs, namely, the silicon oxide and aluminum oxide contained in coal fly ash react with the calcium hydroxide in blast furnace cement, which increases the specific surface area and compression strength of the GCA. A previous study found that GCA can remove hydrogen sulfide from the liquid phase with oxidation by the manganese oxide present on the GCA (6).

GCA was used to remove hydrogen sulfide from eutrophic coastal marine sediments, as it has a harmful impact on aquatic ecosystems in the lower range of 2.93–59 μM (8). Hydrogen sulfide is generated by sulfate-reducing bacteria under the anoxic conditions created by the consumption of dissolved oxygen (DO) by oxidative decomposition of the sediments. High concentrations of hydrogen sulfide are especially detected in marine sediments in enclosed or semi-enclosed water bodies located adjacent to large metropolitan areas (9-15).

GCA was scattered in the water or mixed with organically enriched sediment along the seacoast and was found to suppress hydrogen sulfide effectively (14, 16); moreover, the applied GCA in actual field sites need not be collected because the adsorption site on the GCA for hydrogen sulfide is regenerated through manganese oxidation under oxic conditions such as occur during the vertical mixing seasons (14).

In a previous study, batch experiments for hydrogen sulfide removal were conducted under conditions of dissolved oxygen (DO) less than 2 mg L^{-1} (17). However, the DO at the sea bottom, which has significant organic matter loads, ranges from aerobic to anaerobic conditions. For example, DO ranges of 0.1–19.8 mg L^{-1} at Dokai Bay, Japan (18), 3.78–9.11 mg L^{-1} at Jinhae Bay, Korea (19), 0.14– >4.4 mg L^{-1} at Helena Bay, South Africa (20) and < 2.8–12 mg L^{-1} at Tokyo Bay, Japan (21) have been reported. Hence, it is necessary to evaluate the removal efficiency of hydrogen sulfide by GCA under different DO concentrations to control hydrogen sulfide in coastal marine sediments. The purpose of this study was to evaluate the removal rate of hydrogen sulfide by GCA under aerobic and anaerobic conditions.

2. Experimental

2-1 The Granulated Coal Ash used in this study

Coal which is the origin of fly ash was mainly imported from Australia and Republic Indonesia. GCA tested in this study was produced through the granulation process of pulverized fly ash from Shinonoda thermal electric power stations (Chugoku Electric Power) with added blast furnace cement (B class: Nippon Steel & Sumikin Blast Furnace Slag Cement) as binder amounting to 13% of the final product. GCA granules with 5-mm diameters are mainly composed of silicon oxide, carbonate, aluminum oxide, calcium oxide, organic carbon and iron oxide with a quartz and aluminosilicate crystal phase. The chemical composition of the manufactured GCA, by weight, was 39.5% silicon, 13.3% carbonate, 12.6% Al_2O_3, 5.5% CaO, 2.3% Fe_2O_3, 0.8% MgO, 0.6% K_2O, 0.6% TiO_2, 0.3%Na_2O, 0.2% P_2O_5, and other trace substances **Table 1** (6). The environmentally regulated substances dissolved from the GCA used in this study were well below the standard levels for environmental criteria in Japan (22).

2-2 Hydrogen sulfide removal experiments

The conditions of the removal experiments for hydrogen sulfide with different DO levels and hydrogen concentrations are shown in **Table 2**. The experiments at DO <0.2 mg L^{-1} and 8 mg L^{-1} represent anaerobic and aerobic conditions, respectively. DO of 4 mg L^{-1} represents an intermediate condition.

2-2-1 Anaerobic and intermediate conditions

The hydrogen sulfide solution was prepared as follows: An aliquot of 1 mol $L^{-1}$of Tris-HCl buffer (Kanto Kagaku) was diluted by pure water to be 30 mmol L^{-1}. The 30 mmol L^{-1} of Tris-HCl buffer was de-aerated with N_2 gas to a final DO of < 0.2 mg L^{-1} or 4 mg L^{-1}. The following procedure was conducted in a glove box which was substituted by N_2 gas. An aliquot of $Na_2S•9H_2O$ (Wako Pure Chemical Industries) was dissolved into the 30 mmol L^{-1} of Tris-HCl buffer solution to represent the possible range in the pore water of organically enriched sediments. The pH of the solution was adjusted to 8.2, which is the typical pH of seawater, by adding HCl or NaOH as necessary. Fifty mL of the prepared hydrogen sulfide solution was slowly dispensed into a 100-mL vial bottle, and 0.2 g of the GCA was added to the solution. Thereafter, the bottle was plugged with a rubber cork and sealed with an aluminum cap. The bottle was taken from the glove box and vacuum packed. The bottle was agitated moderately at 100 rpm at 25 ^{o}C in a constant-temperature oven. The batch experiments were conducted in triplicate and the bottles were individually prepared for each sampling time. Time courses of hydrogen sulfide concentration were measured using a detection tube (200SA or 200SB: Komyo Rikagaku Kougyo). Hydrogen sulfide solution was also prepared without the addition of GCA as a control, and experiments were conducted by the same protocol.

2-2-2 The aerobic condition

An aliquot of $Na_2S•9H_2O$ (Wako Pure Chemical Industries) was dissolved into 30 mmol L^{-1} of Tris-HCl buffer solution, which was not de-aerated with N_2 gas, and the DO was approximately 8 mg L^{-1}, to prepare 10 mg-S L^{-1} of hydrogen sulfide concentration. The pH of the solution was adjusted to 8.2, which is the general pH of seawater, by adding HCl or NaOH as necessary. Fifty mL of the prepared hydrogen sulfide solution was slowly dispensed into a 100-mL vial bottle, and 0.2 g of GCA was added to the solution. Thereafter, the bottle was plugged with a rubber cork, sealed with an aluminum cap and vacuum packed. The bottle was agitated moderately at 100 rpm at 25 ºC in a constant-temperature oven. The bottles for this batch experiment were individually prepared for each sampling time. The time courses of hydrogen sulfide concentration were measured using a detection tube (200SA or 200SB: Komyo Rikagaku Kougyo). The hydrogen sulfide solution was also prepared without the addition of GCA as a control, and experiments were conducted by the same protocol.

2-3 Other parameters

The Eh (Electric potential of the normal hydrogen electrode) and pH of initial conditions were measured by an Eh meter (HM-31P: DKK-TOA) and a pH meter (HM-32P: DKK-TOA), respectively.

An Eh–pH diagram of sulfur was drawn using the geochemical modeling software, Geochemist's Workbench 8.0 (RockWare). The parameters used in this thermodynamic calculation were as follows: the activities referred to the liquid-phase concentration of hydrogen sulfide. The pressure and temperature were set at 1.013 hPa and 25 °C, respectively. The Eh-pH diagram of sulfur was almost the same in the hydrogen sulfide range of 2–130 mg-S L^{-1}.

Multiple-comparison analyses were carried out to detect significant differences in the obtained data by Fisher's least significant difference method using the statistical software Excel-Toukei (BellCurve).

3. Results and discussion

3.1 Removal kinetics of hydrogen sulfide by GCA under anaerobic conditions

In the case of hydrogen sulfide initial concentration of 2 mg L^{-1} under DO <0.2 mg L^{-1}, the H_2S concentration of control without GCA decreased to 1.3 mg-S L^{-1} after 24 h due to oxidation (**Fig. 1**). Because the Eh of the solution was -80 mV, the most thermodynamic stable sulfur species is hexavalent (**Fig. 2)**, indicating that the hydrogen sulfide was easy to oxidize. In contrast, the hydrogen sulfide concentration decreased to 0.2 mg-S L^{-1} after 24 h with addition of GCA (**Fig. 1**). Applying GCA significantly decreased the concentration of hydrogen sulfide compared to the control. When the initial concentrations of hydrogen sulfide were 10 or 130 mg-S L^{-1} under DO <0.2 mg L^{-1}, the hydrogen sulfide of the controls decreased to 7.6 mg-S L^{-1} after 24 h and 110 mg-S L^{-1} after 72 h, respectively (**Figs. 1 and 3**). This decrease of hydrogen sulfide concentration was due to oxidation because the Eh values of these solutions were -113 mV and -178 mV, respectively (**Fig. 2**), and the most thermodynamically stable sulfur species was hexavalent. In the case of 10 mg-S L^{-1} of hydrogen sulfide with addition of GCA, the hydrogen sulfide decreased to 2.7 mg-S L^{-1}, lower than that of the control. In the case of 130 mg-S L^{-1}, the concentration of hydrogen sulfide decreased to 91 mg-S L^{-1} after 48 h (**Fig. 3**). However, the hydrogen sulfide concentration did not decrease after 48 h and reached a steady state. The maximum removal of hydrogen sulfide by the GCA was 5.1 mg-S g^{-1} under the DO < 0.2 mg L^{-1}, which was low compared to the previous report (>108 mg-S g^{-1}) obtained under ten times the amount of DO, DO < 2 mg L^{-1} (17). This difference in the maximum removal might be explained by the fact that the manganese oxide which oxidizes hydrogen sulfide to sulfur could not be regenerated under the anaerobic condition, DO < 0.2 mg L^{-1} (14).

3.2 Removal kinetics of hydrogen sulfide by the GCA under different DO concentrations

The removal kinetics of hydrogen sulfide by GCA under different DO concentrations is shown in **Fig. 4**. The hydrogen sulfide concentration of the control decreased to 7.2–7.6 mg-S L^{-1} after 24 h due to oxidation. The hydrogen sulfide concentration after 24 h was not statistically different between different DO concentrations. On the other hand, hydrogen sulfide with addition of GCA decreased with increasing DO concentrations.

After 24 h, hydrogen sulfide concentrations with addition of the GCA were 2.7 mg-S L^{-1} for <0.2 mg L^{-1} DO, 0.9 mg-S L^{-1} for 4 mg L^{-1} DO and <0.1 mg-S L^{-1} for 8 mg L^{-1} DO, respectively. The Eh of the hydrogen sulfide solution with different DOs was -127 mV, -110 mV and -90 mV for DO<0.2 mg L^{-1}, 4 mg L^{-1} and 8 mg L^{-1}, respectively. As shown in **Fig. 2**, hexavalent sulfur was thermodynamically stable with increasing Eh. Therefore, it was considered that the increasing Eh with increasing DO had a cumulative effect on the oxidation of sulfur by the GCA.

3.3 **Removal rate of hydrogen sulfide**

The removal rate of hydrogen sulfide by the GCA is empirically expressed as the first-order equation described by Eq. 1 (correlation of determination; r^2=0.922 to 0.994; **Fig. 5**). The first-order rate constant for hydrogen sulfide was calculated within a range of contact time that did not reach steady state, namely, 0–12 h for an initial hydrogen sulfide concentration of 2 and 10 mg-S L^{-1} and 0–48 h for of 130 mg-S L^{-1}, respectively.

$$[C_t] = [C_0]e^{-kt} \quad \cdot\cdot\cdot (1)$$

The initial rate (V_i :mg-S L^{-1} h^{-1}) for removal of hydrogen sulfide is also defined by Eq. 2.

$$V_i = k \times [C_0] \quad \cdot\cdot\cdot (2)$$

where $[C_t]$ is the concentration of hydrogen sulfide at time t (mg-S L^{-1}), $[C_0]$ is the initial concentration of hydrogen sulfide (mg-S L^{-1}), t is time (h), and k is the rate constant for removal of hydrogen sulfide (h^{-1}).

The rate constant for removal of hydrogen sulfide with and without the addition of GCA is shown in **Fig. 6**. The rate constant for 2 or 10 mg-S L^{-1} of hydrogen sulfide with the addition of GCA was significantly higher than that of the control (statistical significance level; $p<0.01$), indicating that hydrogen sulfide was removed by the GCA. In the case of 130 mg-S L^{-1} of hydrogen sulfide, although the rate constant with GCA was approximately double compared to the control, the statistical significance level was 0.07. The rate constant for removal of hydrogen sulfide by the GCA increased with deceasing initial concentration of hydrogen sulfide (statistical significance level; $p<0.01$). This change of the rate constant for removal of hydrogen sulfide was attributed to the change in Eh of the hydrogen sulfide solution. The Eh of the hydrogen sulfide solution with different concentrations was -113 mV, -127 mV and -178 mV for 2 mg-S L^{-1}, 10 mg-S L^{-1} and 130 mg-S L^{-1}, respectively. Hence, the redox potential for oxidation of hydrogen sulfide increased as the Eh of the hydrogen sulfide solution was high.

The initial rate for removal of hydrogen sulfide did not show statistical difference between initial hydrogen sulfide concentrations of 2 mg-S L^{-1} and 10 mg-S L^{-1} (**Fig. 7**). On the other hand, the initial rate for removal of hydrogen sulfide at a concentration of 130 mg-S L^{-1} was significantly higher than the others ($p<0.01$).

In the next section, we discuss the effect of DO on the rate constant for removal of hydrogen sulfide. The rate constant and initial rate for removal of 10 mg-S L^{-1} of hydrogen sulfide with and without addition of the GCA under different DO concentrations is shown in **Fig. 8** and **Fig. 9**, respectively. The rate constant and initial rate with GCA was high compared to the control under all DO concentrations ($p<0.01$). The rate constant and initial rate with GCA did not show a significant difference between DO concentrations of <0.2 mg L^{-1} and 4 mg L^{-1}. However, in the case of the 8 mg L^{-1} of DO, the removal rate and initial rate were higher than that of others ($p<0.01$).

The contribution of removal for hydrogen sulfide by GCA under DO 8 mg L^{-1} was calculated (**Fig. 10**). The contributions of GCA, DO and the multiplier effect (both GCA and DO) were calculated from the removal of hydrogen sulfide by the GCA under DO <0.2 mg L^{-1}, in the control setting under DO 8 mg L^{-1} and by the difference between removal of hydrogen sulfide by the GCA under DO 8 mg L^{-1} and the sum of the GCA under the DO <0.2 mg L^{-1} and the control setting under DO 8 mg L^{-1}. The contribution percentage of DO did not change significantly and was 20–25%. In the case of the GCA and multiplier effect, the contribution percentage of GCA increased with increasing contact time (15 to 58%) and accordingly that of the multiplier effect decreased (60 to 20%). The multiplier effect considered that increasing Eh with increasing DO, which accelerated the hydrogen sulfide oxidation and regeneration by DO of manganese oxide, which could oxidize hydrogen sulfide.

Conclusions

Granulated coal ash (GCA) could remove hydrogen sulfide in liquid phase under both anaerobic and aerobic conditions. However, the maximum removal of hydrogen sulfide by GCA was 5.1 mg-S g^{-1} under anaerobic conditions, which was low compared to the previous report (DO < 2 mg-S L^{-1}) because the manganese oxide which oxidizes hydrogen sulfide to sulfur could not be regenerated under the anaerobic condition. By contrast, the rate constant for hydrogen sulfide under aerobic conditions (DO 8 mg L^{-1}) was high compared to DO less than 4 mg L^{-1} due to the multiplier effect attributed to both the increasing Eh and the regeneration of manganese oxide by DO.

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Figures

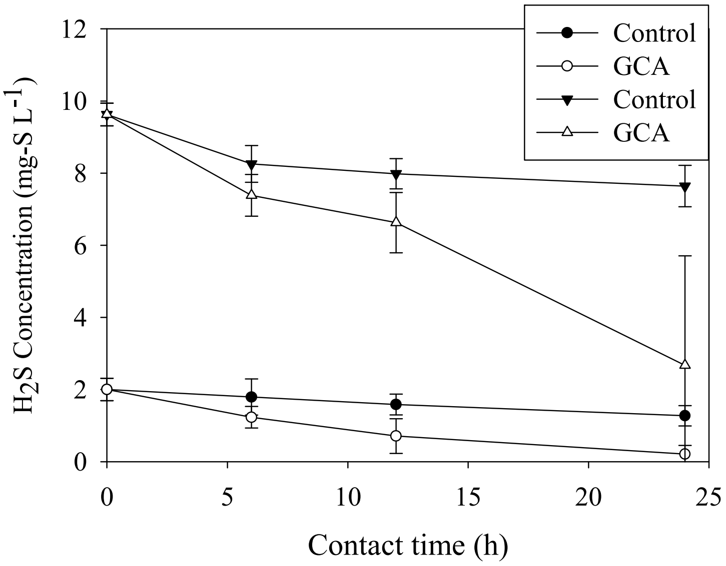

Fig. 1 Time course of hydrogen sulfide after addition of the GCA under DO < 0.2 mg L^{-1}

Initial concentrations of hydrogen sulfide were 2 and 10 mg-S L^{-1}. Error bars show standard deviations.

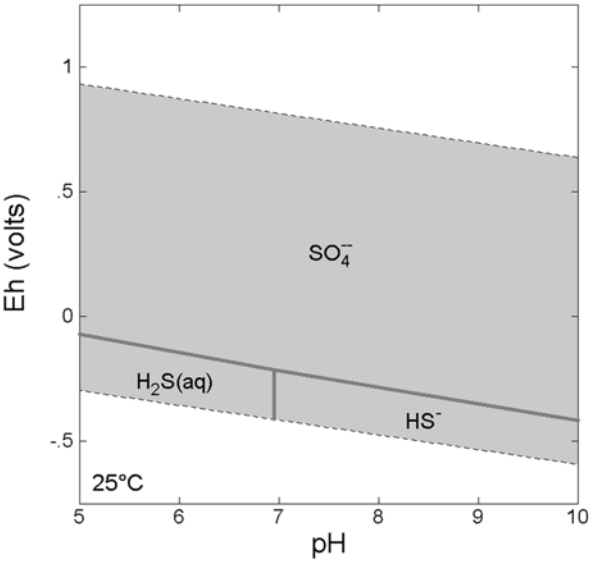

Fig. 2 Eh and pH diagram for sulfur

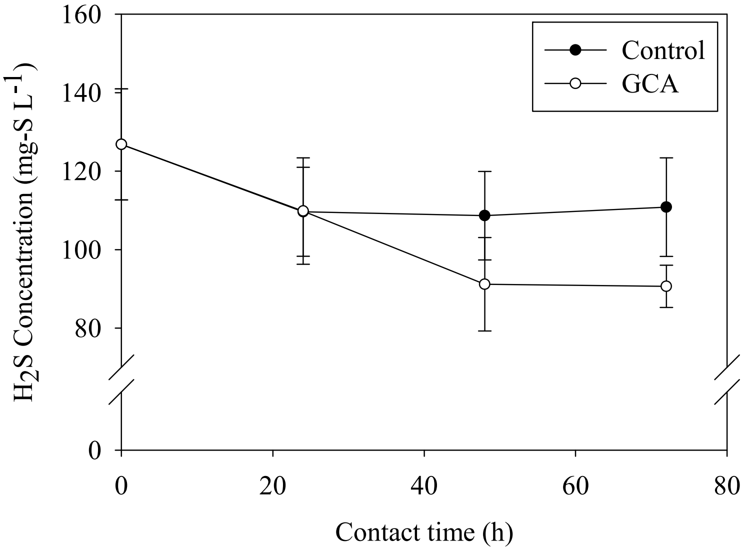

Fig. 3 Time course of hydrogen sulfide after addition of the GCA under DO < 0.2 mg L^{-1}

Initial concentration of hydrogen sulfide was 130 mg-S L^{-1}. Error bars show standard deviations.

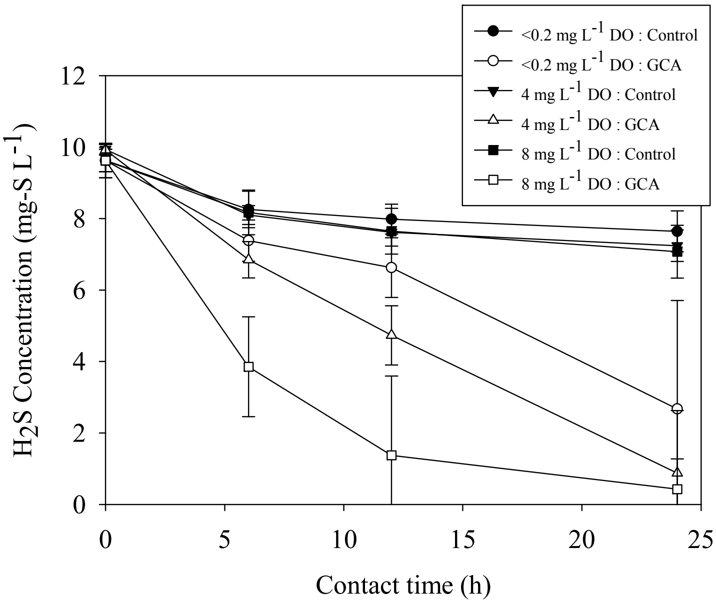

Fig. 4 Time course of hydrogen sulfide after addition of the GCA under different DO concentrations

Initial concentrations of hydrogen sulfide were 10 mg-S L^{-1} Error bars show standard deviations.

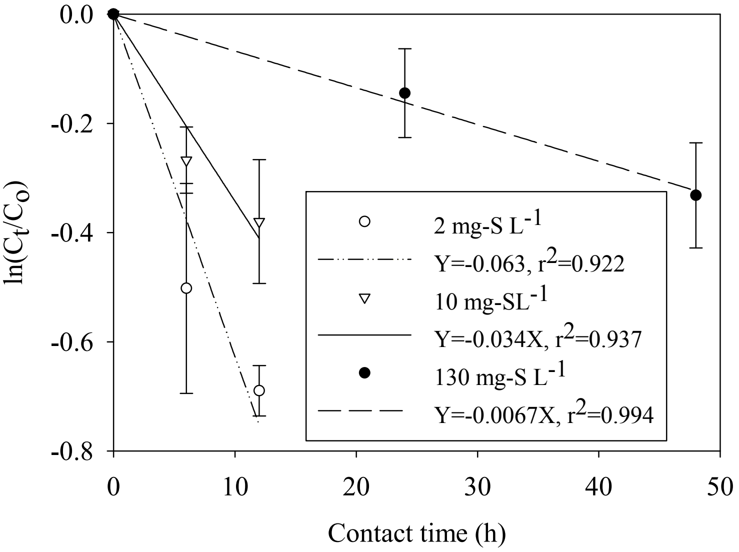

Fig. 5 The first-order removal kinetics of hydrogen sulfide by the GCA

Error bars show standard deviations.

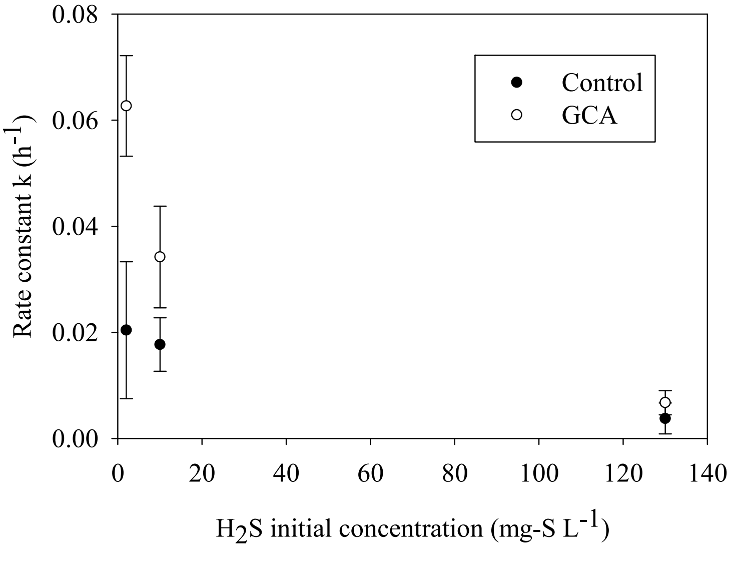

Fig. 6 Rate constant for removal of hydrogen sulfide with and without GCA (control) under DO<0.2 mg L^{-1}.

Error bars show standard deviations.

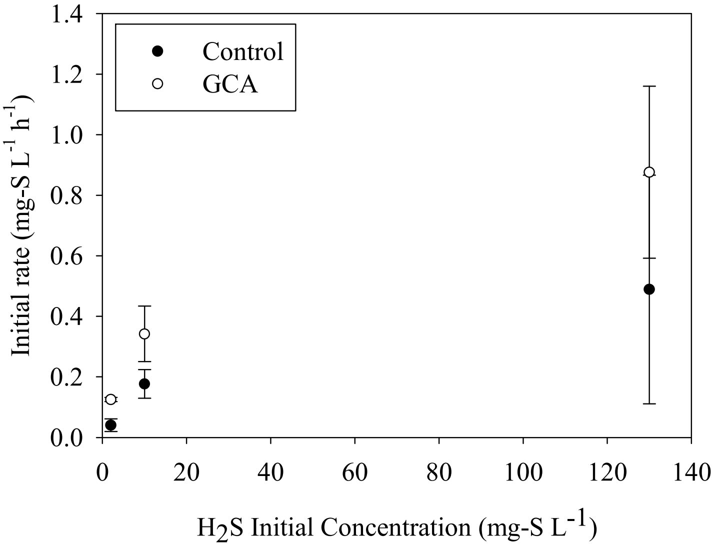

Fig. 7 Initial rate for removal of hydrogen sulfide with and without GCA (control) under DO<0.2 mg L^{-1}.

Error bars show standard deviations.

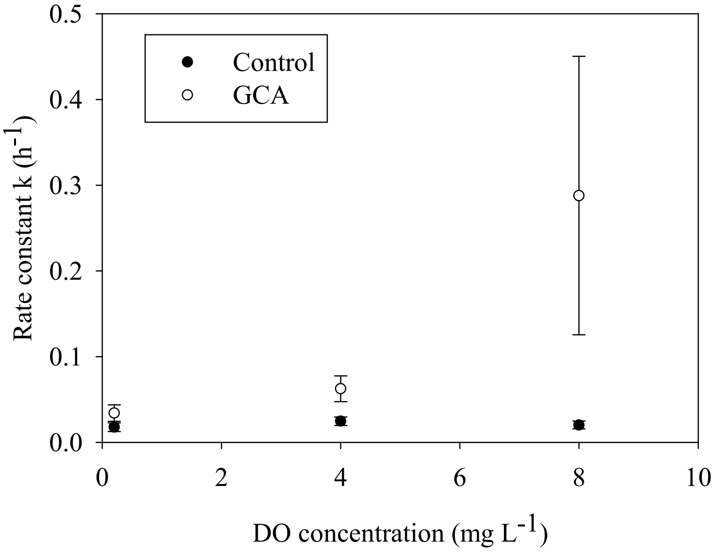

Fig. 8 Rate constant for removal of hydrogen sulfide with and without GCA (control) under different DO concentrations

Initial hydrogen sulfide concentration was 10 mg-S L^{-1}. Error bars show standard deviations.

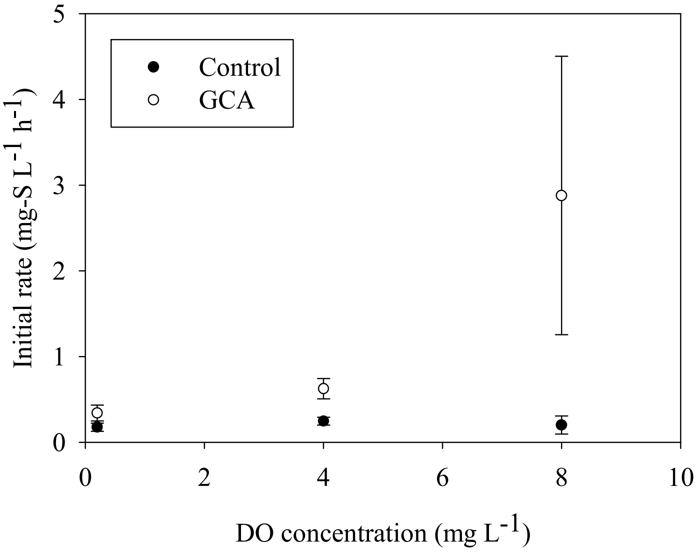

Fig. 9 Initial rate for removal of hydrogen sulfide with and without GCA (control) under different DO concentrations

Initial hydrogen sulfide concentration was 10 mg-S L^{-1}. Error bars show standard deviations.

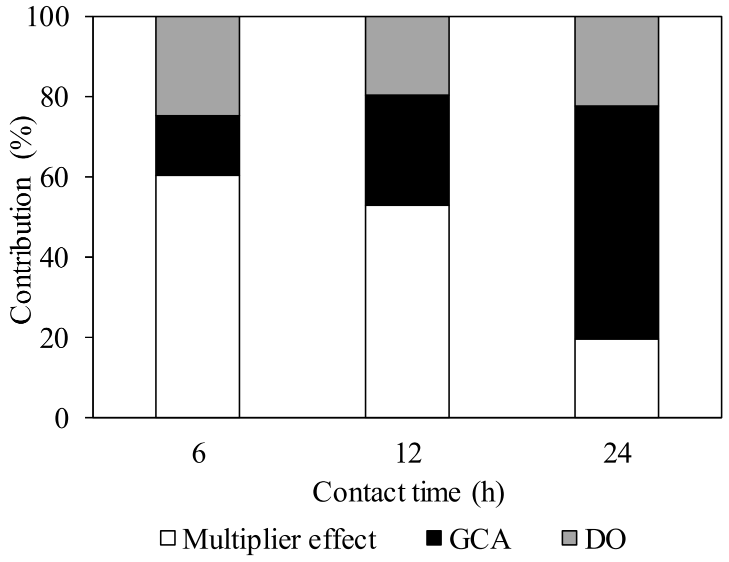

Fig. 10 The contribution of removal for hydrogen sulfide by the GCA

DO concentration and initial hydrogen sulfide concentration were 8 mg L^{-1} and 10 mg-S L^{-1}, respectively.

Tables

Table 1 Trace substances composition of the GCA (mg kg^{-1} dw)

Ba	397	Ni	29.2
Zr	298	Rb	28.8
Mn	255	Co	28.6
N	200	Cr	27.2
V	111	Ga	20.6
Zn	88.9	Sc	14.5
Ce	69.7	Th	12.7
Cu	58.9	Hf	6.7
Y	52.6	W	5.2
Nd	34.4	U	4.2
La	34.2	Yb	3.9
Pb	29.3	Cs	3.2

Table 2 Conditions of removal experiment for hydrogen sulfide

H_2S Concertation(mg-S L^{-1})	DO concentration (mg L^{-1})
2	<0.2
10	<0.2
	4
	applox. 8
130	<0.2