



## Regeneration of manganese oxide as adsorption sites for hydrogen sulfide on granulated coal ash

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### HIGHLIGHTS

- The regeneration of adsorption site for H<sub>2</sub>S on granulated coal ash (GCA) was studied.
- Manganese oxide is an adsorption site for H<sub>2</sub>S on the GCA.
- Manganese oxide was reduced and coupled with H<sub>2</sub>S oxidation under anoxic condition.
- Reduced manganese oxide was oxidized or regenerated under oxidic condition.
- The regenerated manganese oxide could adsorb and oxidize H<sub>2</sub>S.

### ARTICLE INFO

#### Article history:

Received 26 March 2014

Received in revised form 2 June 2014

Accepted 3 June 2014

Available online 12 June 2014

#### Keywords:

Coal-fired power plant

Eutrophication

Manganese oxide

Recycled materials

Sulfur

XAFS

### ABSTRACT

It is important to remove hydrogen sulfide to maintain healthy ecosystems as well as viable aquaculture activities in enclosed water bodies. Granulated coal ash with high adsorption capacity for hydrogen sulfide is a by-product generated from coal combustion processes in coal-fired power plants. The purposes of this study were to (1) verify the regeneration of the adsorption sites for hydrogen sulfide on the granulated coal ash by redox reaction which changes between oxidic and anoxic conditions and (2) prove the regeneration mechanisms of the adsorption site which leads to high adsorption capacity for hydrogen sulfide. XAFS analyses of the granulated coal ash revealed that the adsorption site for hydrogen sulfide on the granulated coal ash was regenerated at least 10 times through oxidation of manganese oxide under oxidic conditions. A positive correlation ( $r = 0.995$ ) between the peak top energy of manganese XAFS in the GCA collected from field trial sites and the Eh of the sediments applied with the GCA was observed. These results proved that hydrogen sulfide was adsorbed and oxidized by the granulated coal ash during the stratified season. During the vertical mixing seasons, oxygen regenerates the adsorption site for hydrogen sulfide. It is concluded that this regeneration of adsorption site gives the granulated coal ash high adsorption capacity for hydrogen sulfide.

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### 1. Introduction

Eutrophication is one of the most serious environmental problems in enclosed water bodies. The excessive terrigenous nutrient loads as well as nutrient dissolution from eutrophic sediments lead to massive growth of algae. As a result, hypoxic water is induced due to the decomposition of the dead cells in stratified seasons.

Under such anoxic condition, hydrogen sulfide is produced through the reduction of sulfate ions by sulfate-reducing bacteria. Hydrogen sulfide is harmful for living organisms, and also consumes oxygen when it is oxidized. It exerts a negative impact on aquatic organisms even at low concentrations of 0.1–2 mg L<sup>-1</sup>, because it interferes with cytochrome c oxidase, the last enzyme of the electron transport system [1,2]. However, a high level of hydrogen sulfide is observed in eutrophic marine sediment pore water throughout the world [3–6]. Therefore it is very important to reduce the hydrogen sulfide concentration in eutrophic sediments so as to maintain healthy ecosystems and aquaculture activities.

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Granulated coal ash (GCA) is a by-product generated from coal combustion processes in coal-fired power plants. Previous studies have proven that GCA adsorbed effectively hydrogen sulfide. The removal mechanism of hydrogen sulfide was possible through oxidation by manganese oxide on the GCA [7]. The GCA has a high adsorption capacity [8] of  $108 \text{ mg S g}^{-1}$  for hydrogen sulfide compared to other materials such as  $37.5 \text{ mg S g}^{-1}$  for noncarbonated steel slag [9], and  $12 \text{ mg-S g}^{-1}$  for crushed oyster shells [10],  $2.3\text{--}71 \text{ mg-S g}^{-1}$  for activated carbons [11,12]. Furthermore, the GCA applied into the sediment in enclosed water bodies at a field experiment site has suppressed hydrogen sulfide for over 5 years. On the other hand, it has been demonstrated that conventional methods such as sand coverage could suppress hydrogen sulfide for a few years. Given that the GCA has such a high adsorption capacity for hydrogen sulfide, this long term suppression observed in the field experiment site might be considered as regeneration of the adsorption sites for hydrogen sulfide under natural conditions which change between oxic to anoxic conditions annually. During the stratified seasons (summer), the bottom layer of the water column in eutrophic enclosed water bodies is in a reduced, or anoxic condition due to the consumption of dissolved oxygen through the decomposition of organic matter. When moving into the vertical mixing seasons (spring and autumn), oxygen is introduced into the bottom of the water column with vertical mixing and hypoxic water disappears. We then developed a hypothesis as follows: the GCA on the manganese oxide oxidizes hydrogen sulfide with coupling reduction of manganese oxide under reduced condition. The reduced manganese oxide on the GCA might be oxidized again, in other words, regenerated by dissolved oxygen during the vertical mixing seasons.

The purpose of this study was to reveal the regeneration of the adsorption sites by proving redox reaction on the surface of the granulated coal ash using XAFS.

## 2. Materials and methods

### 2.1. Granulated coal ash

The GCA with 5 mm diameter tested in this study is produced through the granulation process of coal fly ash from coal used in thermal electric power stations (Chugoku Electric Power) with added cement as binder amounting to approximately 15% of the final product. It is mainly composed of  $\text{SiO}_2$ ,  $\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , organic carbon, and  $\text{Fe}_2\text{O}_3$  with quartz and aluminosilicate crystal phase, and their concentrations are 395, 133, 126, 55.4, 27.4, and  $22.5 \text{ g kg}^{-1}$ , respectively.  $\text{TiO}_2$  and  $\text{MnO}$  contents are  $5.68 \text{ g kg}^{-1}$  and  $329 \text{ mg kg}^{-1}$ , respectively [7]. The environmentally regulated substances dissolved from the GCA used in this study were obviously below the standard levels for environmental criteria in Japan [13].

### 2.2. Removal experiments for hydrogen sulfide

The hydrogen sulfide solution was prepared as follows: Tris-HCl buffer (Kanto Kagaku) was diluted with ultrapure water to prepare  $30 \text{ mmol L}^{-1}$  of buffer solution ( $\text{pH} = 8.2$ ). The buffer solution was deaerated with  $\text{N}_2$  gas. Successively, an aliquot of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (Wako Pure Chemical Industries) was dissolved to make a 10 or  $100 \text{ mg-S L}^{-1}$  hydrogen sulfide solution representing the possible range in the pore water of organically enriched sediments. The batch experiments were conducted in triplicate. Fifty milliliter of the hydrogen sulfide solution was slowly dispensed into a 100 mL DO bottle, and 0.2 g of the GCA was added to the hydrogen sulfide solution. Thereafter, the head space of the bottle was replaced with  $\text{N}_2$  gas and capped tightly using grease for vacuum

use. In the case of samples treated with an initial concentration of  $10 \text{ mg-S L}^{-1}$ , the 100 mL vial bottles sealable by a rubber cork with an aluminum cap were used instead of the DO bottles in order to improve sealed conditions. Thereafter, it was agitated moderately at 100 rpm at  $25^\circ\text{C}$  in a constant-temperature oven for 24 h under anoxic condition. The time courses of hydrogen sulfide concentration were measured using a detection tube (200SA or 200SB; Komyo Rikagaku Kougyo). The detection tube can measure aqueous hydrogen sulfide concentration in sulfur equivalent with forming a brown color band length. After 24 h, the hydrogen sulfide solution was replaced by 50 mL of  $30 \text{ mmol L}^{-1}$  Tris-HCl buffer solution ( $\text{pH} 8.2$ ) and the cap of the bottle was also replaced by a silicon plug to allow exchange of gases. Thereafter, it was agitated moderately at 100 rpm at  $25^\circ\text{C}$  in the constant-temperature oven for 24 h under oxic condition. After 24 h, the Tris-HCl buffer solution was replaced again by 50 mL of hydrogen sulfide solution described above. This removal experiments for hydrogen sulfide were continued repeatedly following the steps in Fig. 1. Control experiments were also carried out without the GCA. The amount of removal sulfur,  $X \text{ (mg g}^{-1}\text{)}$  with the GCA was calculated followed by Eq. (1).

$$X = \frac{(C_b - C_g) * V}{G} \quad (1)$$

where,  $X$ ,  $C_b$ ,  $C_g$ ,  $V$  and  $G$  were the amount of removal sulfur ( $\text{mg g}^{-1}$ ), the concentration of hydrogen sulfide at time  $t$  in the blank ( $\text{mg L}^{-1}$ ), the concentration of hydrogen sulfide at time  $t$  in the GCA bottle ( $\text{mg L}^{-1}$ ), liquid phase volume (0.05 L) and the amount of the GCA (0.2 g).

The precipitation observed in this removal experiments was collected by filtering through a membrane filter (Omnipore: Millipore) with a pore size of  $0.45 \mu\text{m}$ . The precipitate was dried in a nitrogen gas atmosphere and thereafter kept in a vacuum-sealed packing before XAFS analyses.

In order to quantify sulfate and thiosulfate ion desorbed from the GCA under oxic conditions, sulfate and sulfite ion in the solution was measured by an ion chromatograph (ELITE LaChrom: HITACHI) attached with an anion column (#2470;  $4.6 \text{ mm } \phi \times 150 \text{ mm}$ : HITACHI) and a conductivity detector (L-2470: HITACHI). The solution was beforehand filtered through a  $0.45 \mu\text{m}$  syringe filter (Millex: Millipore) and diluted 10 times with ultrapure water to prevent analytical interference of the Tris-HCl buffer solution.

The GCA reacted with  $100 \text{ mg L}^{-1}$  of the initial hydrogen sulfide concentration was analyzed by XAFS as described below.

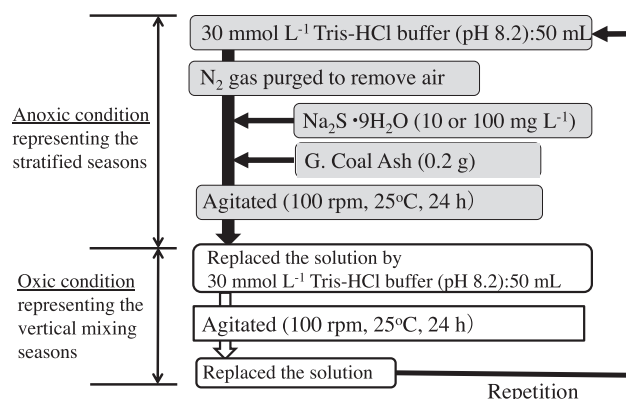


Fig. 1. Flow diagram of hydrogen sulfide removal experiments with the GCA.

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