



## Combined adsorption and oxidation mechanisms of hydrogen sulfide on granulated coal ash

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### ABSTRACT

Hydrogen sulfide is highly toxic to benthic organisms and may cause blue tide with depletion of dissolved oxygen in water column due to its oxidation. The purpose of this study is to reveal the combined adsorption and oxidation mechanisms of hydrogen sulfide on granulated coal ash that is a byproduct from coal electric power stations to apply the material as an adsorbent for hydrogen sulfide in natural fields. Sulfur species were identified in both liquid and solid phases to discuss removal mechanisms of the hydrogen sulfide with the granulated coal ash. Batch experiments revealed that hydrogen sulfide decreased significantly by addition of the granulated coal ash and simultaneously the sulfate ion concentration increased. X-ray absorption fine structure analyses showed hydrogen sulfide was adsorbed onto the granulated coal ash and successively oxidized by manganese oxide (III) contained in the material. The oxidation reaction of hydrogen sulfide was coupling with reduction of manganese oxide. On the other hand, iron containing in the granulated coal ash was not involved in hydrogen sulfide oxidation, because the major species of iron in the granulated coal ash was ferrous iron that is not easily reduced by hydrogen sulfide.

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### 1. Introduction

Generally, the sediments lying under enclosed water bodies adjacent to large metropolis are affected by high organic sedimentation fluxes from terrigenous loads and internal cycles attributed to primary production. Organic matter retained on the bottom of enclosed water bodies consumes large amount of dissolved oxygen from the water column through its oxidative decomposition processes. Hypoxic water mass is often formed during the stratified seasons. Under such reduced condition, hydrogen sulfide that is highly toxic to benthic organisms is generated through sulfate reduction by sulfate reducing bacteria. It may also cause depletion of dissolved oxygen in the bottom water due to its oxidation resulting to the deterioration of benthic ecosystems. Since oxygen depletion is fatal to organisms, it sometimes brings much economic losses to aquaculture activities. Therefore, it is very important to reduce the concentration of hydrogen sulfide in sediments so as to maintain healthy ecosystems and provide sustainable aquaculture activities.

Removal or adsorption strategies of hydrogen sulfide are mainly catalytic oxidation [1–4] or formation of sulfide [5,6]. Some metals act as efficient catalysts for hydrogen sulfide oxidation, such as Na<sub>2</sub>CO<sub>3</sub> impregnated coal-based activated carbon [1], bismuth-molybdenum binary oxides [2], Fe/MgO nano-crystals [3], and vanadia-titania aerogel [4]. It was also reported that iron, zinc, and copper species play important roles in the formation of sulfide [5,6].

Granulated coal ash (GCA) is a by-product generated from coal combustion processes in coal thermal electric power stations. In 2007, 12 mega tons of coal ash were generated from coal thermal electric power stations and other industries in Japan [7]. Previous studies have proven that GCA adsorbed effectively hydrogen sulfide in seawater [8]. Accordingly, in container experiments designed for simulating enclosed water bodies, the concentration of hydrogen sulfide in pore water of organically enriched marine sediment mixed together with GCA decreased significantly by 77–100% compared to those without application of GCA [9]. Remarkably, the GCA has quite a high adsorption capacity, 108 mg S g<sup>-1</sup> for hydrogen sulfide compared to other materials [8]. The assumed removal processes of hydrogen sulfide by GCA are the formation of sulfide with trace or sub-trace element contained in GCA and oxidation [8]. However, the exact hydrogen sulfide removal mechanism, namely,

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elements that have contributed toward hydrogen sulfide oxidation reaction, is not fully understood. The purpose of this study is to reveal the combined adsorption and oxidation mechanisms of hydrogen sulfide occurring at the surface of GCA.

## 2. Materials and methods

### 2.1. Granulated coal ash (GCA)

The GCA tested in this study is a commercially sold product, named “Hi-beads” (Energia Eco Materia Co., Inc.) with 5 mm diameter, which is produced through the granulation process of pulverized fly ash from coal firing systems in thermal electric power stations (Chugoku Electric Power) with added cement as binder amounting to 10–15% of the final product. The GCA is mainly composed of SiO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, Al<sub>2</sub>O<sub>3</sub>, CaO, C, and Fe<sub>2</sub>O<sub>3</sub> with quartz and aluminosilicate crystal phase, and their concentrations are 395, 133, 126, 55.4, 27.4, and 22.5 g kg<sup>-1</sup>, respectively (Table 1). TiO<sub>2</sub> and MnO contents are 5.68 g kg<sup>-1</sup> and 329 mg kg<sup>-1</sup>, respectively [10]. The environmentally regulated substances dissolved from the GCA used in this study were obviously below the standard levels for environmental criteria in Japan [10].

### 2.2. Adsorption experiment

Adsorption experiment was carried out in a 100 mL BOD bottle containing 50 mL of the hydrogen sulfide solution with concentrations of 8 and 85 mg S L<sup>-1</sup> that represents possible levels in the pore water of organically enriched marine sediments. The hydrogen sulfide solution was prepared as follows: aliquot of Na<sub>2</sub>S · 9H<sub>2</sub>O (Nacalai Tesque) was dissolved in 500 mL pure water deaerated with N<sub>2</sub> gas. Thereafter, the pH of the solution was adjusted to 8.2 with HCl. Fifty mL of hydrogen sulfide solution was slowly dispensed into the bottle and 0.2 g of the GCA was added to the solution. The amount of GCA is optimized on the basis of the previous study to minimize change of pH [8]. Thereafter, the head space of the bottle was replaced with N<sub>2</sub> gas and capped tightly using grease for vacuum use. The bottle was agitated moderately at 100 rpm at 25 °C in a water bath, and time courses of hydrogen sulfide concentration, pH, and oxidation reduction potential (ORP) were measured with a detection tube (200SA or 200SB: Komyo Rikagaku Kougyo), pH electrode (F-22: Horiba Ltd.), and ORP electrode (RM-20P: DKK-TOA Co.), respectively. The ORP value was converted to Eh value following standard methods [11].

To quantify the sulfur mass balances, sulfate ion concentration was also determined after scavenging remaining hydrogen sulfide with formation of ZnS so as to prevent further oxidation of hydrogen sulfide during analysis. The procedure for scavenging hydrogen

sulfide was partially modified based on Ref. [12]. Briefly, 1 mol L<sup>-1</sup> of Zn(CH<sub>3</sub>COO)<sub>2</sub> · 2H<sub>2</sub>O solution (0.1 mL) and 6 mol L<sup>-1</sup> NaOH solution (0.1 mL) were successively added to 10 mL of sample. After precipitation of ZnS, the supernatant solution was filtered through a hydrophilic PVDF filter with 0.45 μm pore size (MILLEX: Millipore). Thereafter, pH of the filtrates was adjusted to neutral while the concentration of sulfite ion was determined using an ion chromatograph (DX-120: DIONEX) attached with an anion exchange column (Ion Pac AS12A: DIONEX). According to a pretest, the sulfate ion was perfectly recovered (98%) using this proposed method.

An experiment without GCA was also conducted as the control following the same procedure to compensate for hydrogen sulfide loss due to volatilization. These same settings were prepared in triplicates. The GCA treated in 85 mg S L<sup>-1</sup> of hydrogen sulfide solution was submitted to XAFS analyses described below.

### 2.3. X-ray absorption fine structure (XAFS) analyses and data processing

Sulfur and titanium K edge XAFS spectra (ranges 2460–2485 eV for sulfur and 4950–5030 eV for titanium) were measured using the BL11 in Hiroshima Synchrotron Research Center, HiSOR [13]. The synchrotron radiation from a bending magnet was monochromatized with a Si(111) double-crystal monochromator. The sample chamber was filled with He gas, and XAFS spectra were measured both by the X-ray fluorescence yield (XFY) mode using a SDD detector (XR-100SDD; AMPTEK) and conversion electron yield (CEY) mode. The X-ray energies around K edges of sulfur and titanium were calibrated with the spectra of CuSO<sub>4</sub> and Ti foil obtained with the CEY mode, respectively. The K edge main peak of sulfate was set to 2481.6 eV [14] and the pre-edge peak of Ti foil of K shell was set to 4970.0 eV, respectively. As references, Na<sub>2</sub>SO<sub>4</sub> (Wako Pure Chemical Industry), Na<sub>2</sub>SO<sub>3</sub> (Wako Pure Chemical Industry), FeS<sub>2</sub> (Stream Chemicals), FeS (Wako Pure Chemical Industry), Al<sub>2</sub>S<sub>3</sub>, (Sigma-Aldrich), TiS<sub>3</sub> (Alfa Aesar), MnS (Sigma-Aldrich), CaS (Sigma-Aldrich), Ti foil (Niraco) were measured by the CEY mode. The pieces of relatively flat GCA samples were mounted on a double-stick tape (NW-K15; Nichiban) placed in the central hole (15 mm in diameter) of a copper plate. The surface of the sample was attached to that of the copper plate. The angle between the incident X-ray and the sample surface was adjusted at 20°, and the X-ray fluorescence was detected from the direction normal to the incident beam in the plane of electron orbit of the storage ring.

Manganese and iron K edge XAFS spectra (range 6400–6725 eV for manganese and range 7080–7250 eV for iron) were measured in BL3 st the Ritsumeikan SR center, Japan. The synchrotron radiation was monochromatized with a Si(220) double-crystal monochromator. The sample XAFS spectra were measured by X-ray fluorescence yield mode using a three-elements Ge solid state detector, SSD (GUL0110S: Canberra). Samples were sealed with polypropylene film and they were positioned at 45° to the incident beam in fluorescence mode. The X-ray energy was calibrated by defining the K edge pre-edge peak of δ-MnO<sub>2</sub> and hematite fixed at 6540 and 7112 eV, respectively.

For manganese standard, δ-MnO<sub>2</sub> (Wako Pure Chemical Industry), Mn<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich), MnSO<sub>4</sub> · 5H<sub>2</sub>O (Wako Pure Chemical Industry), and MnS (Sigma-Aldrich), and for iron standard, hematite (Stream Chemicals), iron hydroxide (III) (Alfa Aesar), FeS<sub>2</sub> (Stream Chemicals), FeO (Alfa Aesar), FeS (Wako Pure Chemical Industry), FeSO<sub>4</sub> · 7H<sub>2</sub>O (Wako Pure Chemical Industry), and iron foil (Alfa Aesar) were also measured by the transmission mode using an ionization chamber filled with mixed gases: Ar 15% and N<sub>2</sub> 85% and for incident chamber (I<sub>0</sub>) and Ar 50% and N<sub>2</sub> 50% for transmitted chamber (I).

The spectra obtained by these XAFS analyses were processed with XAFS spectra processing software (REX2000 ver. 2.5: Rigaku

**Table 1**  
Chemical composition of granulated coal ash.

Main elements	(g/kg dw)	Trace elements (mg/kg dw)			
SiO <sub>2</sub>	395.3	Ba	397	Rb	28.8
CO <sub>3</sub> <sup>2-</sup>	133	MnO	329	Co	28.6
Al <sub>2</sub> O <sub>3</sub>	125.5	Zr	298	Cr	27.2
CaO	55.4	N	200	Ga	20.6
C	27.4	V	111	Nb	34.4
Fe <sub>2</sub> O <sub>3</sub>	22.5	Zn	88.9	Sc	14.5
MgO	8.11	Ce	69.7	Th	12.7
K <sub>2</sub> O	6.09	Cu	58.9	Hf	6.7
H	5.2	Y	52.6	W	5.2
TiO <sub>2</sub>	5.68	Nd	34.4	U	4.2
Na <sub>2</sub> O	2.5	La	34.2	Yb	3.9
P <sub>2</sub> O <sub>5</sub>	1.86	Pb	29.3	Cs	3.2
Sr	0.4	Ni	29.2		

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