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Research Paper

Removal of hydrogen sulfide gas using coal fly ash – blast furnace cement composite

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ABSTRACT

The number of complaints regarding offensive odors from service industries, such as restaurants and garages, has recently increased. In this study, we aimed to develop an adsorbent for hydrogen sulfide gas derived from domestic wastewater and reveal the mechanisms of its removal. The adsorbent used for hydrogen sulfide gas removal was prepared by mixing coal fly ash and blast furnace cement with a mixing ratio of 87:13 by mass percentage. The optimum calcination temperature of the adsorbent was 700 °C to achieve a high removal performance for both dry and humid hydrogen sulfide gas. The X-ray absorption fine structure analysis revealed that hydrogen sulfide was removed on the adsorbent by oxidizing to sulfate. A pilot-scale experiment was conducted to evaluate the removal performance of hydrogen sulfide gas derived from domestic wastewater using the developed adsorbent. For a week, the average removal percentage of hydrogen sulfide gas derived from domestic wastewater remained at 99.1%. Therefore, the developed adsorbent for hydrogen sulfide gas is promising and cost-effective for promoting the recycling of coal fly ash.

Key words: decentralized wastewater treatment system, deodorant, hydrogen sulfide, recycled materials, SDGs, septic tank

HIGHLIGHTS

- Adsorbent for H₂S gas was prepared by mixing coal fly ash and blast furnace cement.
- Adsorbent could remove both dry and humid H₂S gas.
- H₂S was oxidized to sulfate and removed from the adsorbent.
- Average removal percentage of H₂S gas remained at 99.1%.
- This study contributes to sustainable development goals in terms of coal fly ash recycling.

GRAPHICAL ABSTRACT



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INTRODUCTION

The four major offensive odors, ammonia, trimethylamine, methyl mercaptan, and hydrogen sulfide, are regulated under the Offensive Odor Control Law in Japan. Currently, the number of complaints regarding offensive odors from service industries, such as restaurants and garages, has risen to 8,000 per year (Kamigawara 2003). Offensive odors are also generated by lime-stabilized biosolids, such as sewage sludge (Krach *et al.* 2008), pet food, roofing tar, dead animals (Eltarkawe & Miller 2019), urban rivers (Sado-Inamura & Fukushi 2018), and Johkasou, such as a septic tank, a Japanese compact-scale advanced wastewater treatment system (Ichinari *et al.* 2008; Fajri *et al.* 2018).

This study focused on removing hydrogen sulfide (H_2S) which is a highly toxic, colorless gas, with a rotten-egg-like odor. H_2S is generated from hydrocarbon sources, such as natural gas, biogas, crude oil, wastewater treatment, and anoxic sediments (Nassar *et al.* 2016; Asaoka *et al.* 2018; Khabazipour & Anbia 2019). Because H_2S is highly toxic and corrosive, it can cause corrosion of oil and gas pipelines and their devices (Nassar *et al.* 2016), poison catalysts (Khabazipour & Anbia 2019), and pose a serious threat to human health. The odor threshold for human exposure to H_2S is 0.011 mg m^{-3} (Selene & Chou 2003). When H_2S exposure exceeds 2.8 mg m^{-3} , it negatively impacts human health (Selene & Chou 2003). Therefore, to control pollution and protect human health, H_2S must be removed.

In a previous study on the removal of H_2S gas, porous metal oxides such as $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ (Su *et al.* 2017), Co_3O_4 (Wang *et al.* 2017a), three-dimensionally ordered macropore CuO (Wang *et al.* 2017b), ZnO (Tran 2016), and zeolite (Liu & Wang 2017; Yang *et al.* 2018), metal oxide-loaded mesoporous silicas (Montes *et al.* 2013; Wu *et al.* 2017; Cara *et al.* 2018), and Fenton reagent (Wang *et al.* 2019) were proposed. However, these adsorbents require significant preparation costs. A cost-effective adsorbent for removing H_2S gas was developed in this study by mixing coal fly ash, which is a by-product of coal electric power plants and blast furnace cement, to increase the specific surface area through pozzolanic reaction. A coal fly ash-blast furnace cement composite was previously reported to be capable of removing H_2S from both fresh and seawater (Asaoka *et al.* 2012; Asaoka *et al.* 2014; Asaoka *et al.* 2017). However, no data on the removal of H_2S gas by the coal fly ash-blast furnace cement composite are available. This study was aimed to optimize the granulated coal ash to remove H_2S gas derived from domestic wastewater and reveal the mechanisms of H_2S gas removal by the coal fly ash-blast furnace cement composite.

METHODS

Preparing the coal fly ash-blast furnace cement composite

Coal fly ash provided by the Chugoku Electric Power Co., Inc., Japan, was mixed with blast furnace cement (Class B: Nippon Steel Blast Furnace Slag Cement Co., Ltd, Japan) at a mixing ratio of 87:13 by mass percentage. Water was added so that the mixture amounted to 20 wt.%. The mixture was then granulated using a rotary pan-type granulator. Every day for the first week, pure water was sprayed to wet the surface of the granulated composite. The granulated composite was then air-dried in a laboratory at 25°C for at least 4 months to complete the pozzolanic reaction between the coal fly ash and blast furnace cement. The granulated composite was mainly composed of 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 (Asaoka *et al.* 2012). The granulated composite was crushed into a diameter of approximately 5 mm and screened using a sieve into a diameter of 3–5 mm. The composite was calcined for 3 h at temperatures ranging from 300–1,000 $^\circ\text{C}$ to determine the optimum calcination temperature. The Brunauer–Emmett–Teller (BET) specific surface areas of the composites were measured by the adoption of N_2 gas using an advanced micropore size and chemisorption analyzer (Autosorb iQ, Quantachrome Instruments). The granulated composite for thermogravimetry/differential thermal analysis (TG-DTA) was ground using a mortar, rinsed five times with acetone, and dried one day before analyses. TG-DTA was performed using a thermal analyzer (Thermo plus EVO II; Rigaku) at a heating rate of $10^\circ\text{C min}^{-1}$ from 25°C to $1,000^\circ\text{C}$ in an alumina pan under N_2 gas flow (800 mL min^{-1}). The surface pH of the granulated composite was measured using a compact water quality meter (LAQUA twin pH; HORIBA). On the electrode, a CMF filter sheet (Y100A13; Advantec) was installed, and the granulated composite particles were placed on the filter. The surface pH of the granulated composite was then measured by dripping a few drops of ultrapure water on the granulated composite particles.

Removal experiments of H_2S gas

Adsorption experiments were conducted under both dry and humid gas conditions. Under the dry gas condition, approximately 28 g of the granulated composite samples (hereafter adsorbent) was loaded into a polyvinyl chloride column

(31 mm inner diameter \times 50 mm length). To simulate humid conditions in Johkasou (RH:100%), the adsorbent was immersed in water for 1 day and used in the adsorption experiments.

To simulate H_2S derived from wastewater of multiple dwelling houses, convenience stores, restaurants, and food factories, H_2S gas was generated as follows (Supplementary Material, Figure S1): 200 g of sodium sulfide nonahydrate (Kishida Chemical) was added to 400 mL of saturated sodium sulfide nonahydrate solution in 2 L of polyethylene vial. Five milliliters of 10% HCl (Guaranteed Reagent; Kishida Chemical) was dropped into the polyethylene vial every 3 min to generate H_2S gas. Using an air pump, deoxidized air was introduced into the saturated sodium sulfide nonahydrate solution, and the generated H_2S gas was introduced into the column at a rate of 0.3 L min^{-1} . Gas trap bags were installed at the front and rear stages of the column to measure the concentration of H_2S gas before and after the column using detection tubes (4LL, 4 L, and 4HM; Gastech). The laboratory temperature was maintained at approximately 28°C and 1 atm. The generated H_2S gas with an average concentration of 1,000–1,100 ppm was introduced into the column. The adsorption of H_2S gas was calculated using Equation (1).

$$Q(\text{g m}^{-3}) = \frac{V(C_i - C)}{W} \quad (1)$$

where V represents the volume of the feed stream of the H_2S gas to the column (m^3), C_i represents the initial concentration of H_2S gas (g m^{-3}), C represents the concentration of H_2S gas after the column (g m^{-3}), and W represents the weight of the coal fly ash-blast furnace cement composite samples loaded in the column (m^3).

The adsorbent sample for X-ray absorption fine structure (XAFS) analyses to identify the sulfur species adsorbed on the adsorbent was vacuum-packed and stored in a freezer to prevent changes in the chemical species.

Identification of sulfur species adsorbed on the adsorbent

At the Hiroshima Synchrotron Research Center, XAFS analyses were performed to identify the sulfur species adsorbed on the adsorbent using BL11 (HiSOR; Asaoka *et al.* 2012, 2018). The sulfur K-edge spectra (range 2,460–2,490 eV) of the adsorbent were measured using X-ray fluorescence yield mode with an SDD detector (XR-100SDD; AMPTEK) under He atmosphere. The K-edge main peak of sulfate derived from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was calibrated to 2,481.6 eV. The angle between the incident X-ray and the sample surface was adjusted to 20° , and the X-ray fluorescence was detected from the direction normal to the incident beam in the plane of the electron orbit of the storage ring. The obtained XAFS spectra were processed using the XAFS processing software (REX2000 ver. 2.6; Rigaku Co. Ltd).

The Eh–pH diagram of sulfur was illustrated by the geochemical modeling software, Geochemist's Workbench 8.0 (RockWare). The parameters used in this thermodynamic calculation were as follows: the activity of sulfate is set to 0.04 mmol L^{-1} . The pressure and temperature were set at 1.013 hPa and 25°C , respectively.

Pilot-scale experiment on the removal of H_2S gas from domestic wastewater

A schematic of the pilot-scale experiment on the removal of H_2S gas from domestic wastewater is shown in Supplementary Material, Figure S2. Domestic wastewater discharged from a condominium with 12 houses was introduced into 5.6 m^3 of an experimental tank 12 times per day to simulate domestic wastewater-derived H_2S . The total volume of domestic wastewater discharged into the experimental tank and the hydrological residence time were $4 \text{ m}^3 \text{ d}^{-1}$ and 1.25 days, respectively. The domestic water composition was adjusted to biological oxygen demand: 200 mg L^{-1} , total nitrogen: 45 mg L^{-1} , total phosphorus: 5.0 mg L^{-1} , suspended solid: 160 mg L^{-1} , and alkalinity: 190 mg L^{-1} using urea, ethanol, sodium bicarbonate, and potassium dihydrogen phosphate (Guaranteed Reagent; Kishida Chemical). To control and adjust the concentration of suspended solid, toilet paper was added to domestic wastewater. The domestic wastewater-derived gas was introduced into a polyvinyl chloride column (100 mm inner diameter \times 385 mm length) filled with the adsorbent by a blower (EC-75S-R3A3; Showa Denki). The flow rate was controlled at a rate of 50 L min^{-1} using a flow monitor (Eggs DELTA, FLM30-10PCW; Oval). The data logger (GHS-8AT; Gastec) was installed at the front and rear stages of the column to measure the temperature and concentration of H_2S gas derived from the domestic wastewater, and the temperature and concentration of the H_2S gas at the front and rear of the column were measured every 10 min for a week. The average temperature and concentration of H_2S gas derived from domestic wastewater were 14.4°C and 31.0 ppm, respectively.

RESULTS AND DISCUSSION

Optimum calcination temperature

The calcination temperature of the adsorbent prepared in this study was optimized in the range of 300–1,000 °C because the adsorption capacity of the adsorbent without calcination (raw material) for humid H₂S gas decreased significantly to 59 g-H₂S m⁻³ (Figure 1). Supplementary Material, Figure S3 shows the TG-DTA curves of the adsorbents. The decreases in the TG at approximately 120 °C and 120–300 °C correspond to hygroscopic water evaporation, and both crystallization of water and strong physically bonded water removal, respectively (Burdhos Nergis *et al.* 2020). Over 300 °C, the TG decreases, which corresponds to the dehydroxylation of iron, silicon, and aluminum hydroxide groups (Landmesser *et al.* 1997; Fuji & Chikazawa 2000; Laskou *et al.* 2006; Burdhos Nergis *et al.* 2020; Wang *et al.* 2020). The decrease in TG at 550–750 °C corresponds to CaCO₃ decompositions (Duan *et al.* 2017). Based on this, when the calcination temperature was greater than 300 °C, the adsorption capacity of the adsorbent for H₂S gas under humid conditions did not decrease when compared to that under dry conditions (Figure 1). This result indicates that the hydrophobicity of the adsorbent surface increased because of the formation of siloxane and aluminum oxide derived from silanol and alanol group condensation. Hence, H₂S could be adsorbed on the adsorbent without the adsorption interference of water. The adsorption capacity for H₂S gas reached a peak under dry conditions at 600–700 °C under dry conditions and at 700 °C under humid conditions (Figure 1). However, when the calcination temperature exceeded 700 °C, the adsorption capacity for H₂S gas significantly decreased. The significant decrease in the adsorption capacity for H₂S gas was attributed to the decrease in the specific surface area of the adsorbent (Supplementary Material, Figure S4). Without calcination, the specific area of the adsorbent was 25.0 m² g⁻¹, and the values decreased gradually with increasing calcination temperature up to 700 °C. At calcination temperatures over 700 °C, the specific surface area of the adsorbent significantly decreased, corresponding to the decomposition of CaCO₃ (Supplementary Material, Figure S3). Thus, the optimized calcination temperature was 700 °C, and the breakthrough curve of H₂S gas obtained by the calcinated adsorbent at 700 °C is also shown in Figure 2. The breakthrough capacity of the adsorbent was calculated to be 650 g-H₂S m⁻³ under dry conditions and 730 g-H₂S m⁻³ under humid conditions.

Adsorption mechanisms of H₂S gas

In this study, sulfur species adsorbed on the prepared adsorbent were identified to reveal the adsorption mechanisms of H₂S gas by XAFS (Figure 3 and Supplementary Material, Figure S5). Sulfate and elemental sulfur were detected on the adsorbent without calcination and the 500 °C -calcined adsorbent. In the case of the 700 °C and 1,000 °C -calcined adsorbents, sulfate was identified. Sulfur and sulfate are considered to be derived from the oxidation of H₂S (Asaoka *et al.* 2012). When the calcination temperature exceeded 700 °C, H₂S was completely oxidized to sulfate, indicating that the adsorption capacity of H₂S gas reached a peak at 700 °C. This enhancement of oxidation is considered to be caused by an increase in the surface pH of the adsorbent. Supplementary Material, Figure S6 shows the surface pH of the adsorbent calcined at each temperature. The surface pH of the adsorbent without calcination and the adsorbent calcined at 300–500 °C ranged from 8.9 to 9.5. When the calcination temperature was 600 °C, the surface pH of the adsorbent increased by 10.4, reaching a plateau (pH 11.4–12.1) at a calcination temperature of 700–1,000 °C. The increase in the surface pH corresponded to the transformation of CaCO₃ in the

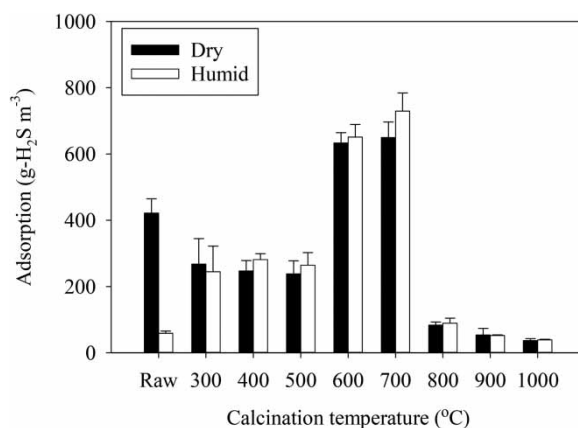


Figure 1 | Effect of calcination temperature on adsorption of hydrogen sulfide gas.

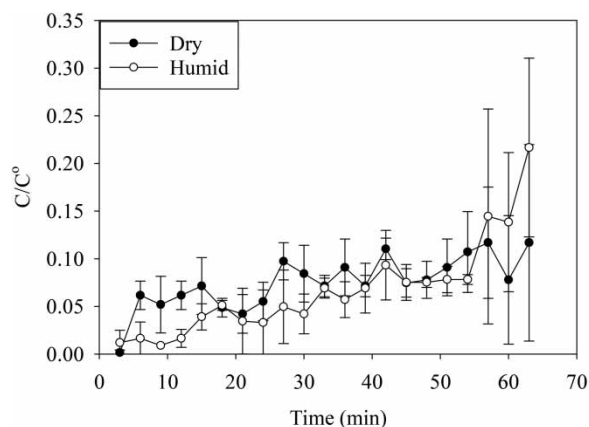


Figure 2 | Breakthrough curves of hydrogen sulfide gas under dry or humid conditions.

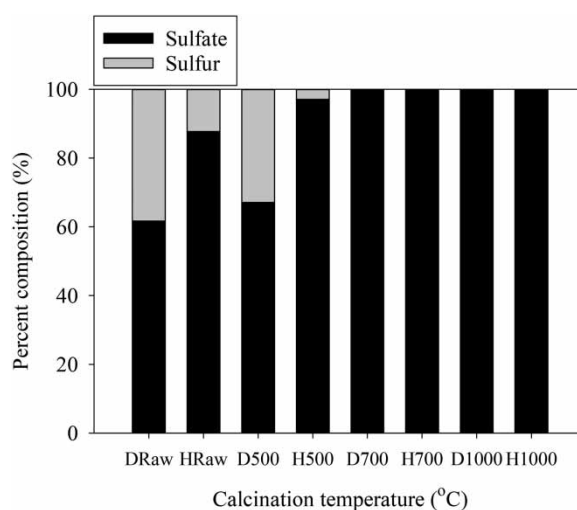


Figure 3 | Percent composition of sulfur species after adsorption of hydrogen sulfide gas on the adsorbent. D: Dry condition; H: Humid condition.

prepared adsorbent to CaO. According to the Eh–pH diagram of sulfur, the redox boundary between sulfate and sulfide thermodynamically shifts toward low Eh with increasing pH (Supplementary Material, Figure S7), indicating that the sulfide on the adsorbent calcined at 700–1,000 °C was completely oxidized to sulfate.

Pilot-scale experiments on the removal of H₂S gas from domestic wastewater

Pilot-scale experiments on the removal of H₂S gas derived from domestic wastewater is shown in Figure 4. The H₂S gas concentration in the control (before a column) ranged from <0.1–93 ppm. During the entire experimental period, the average removal percentage of H₂S gas was 99.1%. The H₂S gas concentration after the adsorbent column ranged from <0.1–0.9 ppm until the cumulative amount of adsorbed H₂S reached 8.4 g at 98.7 h, which corresponded to 98–100% removal of H₂S gas. Thereafter, the H₂S gas concentration after the adsorbent column ranged from <0.1–4.7 ppm, with a removal percentage was 91.1–100%. The H₂S gas removal performance of the adsorbent is considered to have silently decreased as the amounts of H₂S increased.

CONCLUSIONS

The adsorbent for the removal of H₂S gas was developed by mixing coal fly ash and blast furnace cement in a ratio of 87:13 by mass percentage. To achieve a high removal performance for both dry and humid H₂S gas, the optimum calcination

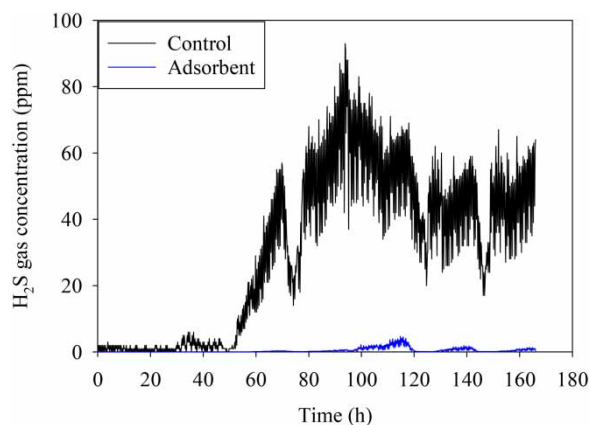


Figure 4 | Hydrogen sulfide gas concentrations from a septic tank before and after introducing the adsorbent column.

temperature was 700 °C. For a week, the average removal percentage of H₂S gas derived from domestic wastewater remained at 99.1%. The mechanism of H₂S removal is primarily oxidation to sulfate. Therefore, the developed adsorbent for H₂S gas in this study is one of the most promising cost-effective adsorbents for promoting the recycling of coal fly ash.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Asaoka, S., Hayakawa, S., Kim, K. H., Takeda, K., Katayama, M. & Yamamoto, T. 2012 Combined adsorption and oxidation mechanisms of hydrogen sulfide on granulated coal ash. *Journal of Colloid and Interface Science* **377** (1), 284–290. <https://doi.org/10.1016/j.jcis.2012.03.023>.
- Asaoka, S., Okamura, H., Akita, Y., Nakano, K., Nakamoto, K., Hino, K., Saito, T., Hayakawa, S., Katayama, M. & Inada, Y. 2014 Regeneration of manganese oxide as adsorption sites for hydrogen sulfide on granulated coal ash. *Chemical Engineering Journal* **254**, 531–537. <https://doi.org/10.1016/j.cej.2014.06.005>.
- Asaoka, S., Okamura, H., Kim, K., Hatanaka, Y., Nakamoto, K., Hino, K., Oikawa, T., Hayakawa, S. & Okuda, T. 2017 Optimum reaction ratio of coal fly ash to blast furnace cement for effective removal of hydrogen sulfide. *Chemosphere* **168**, 384–389. <https://doi.org/10.1016/j.chemosphere.2016.10.070>.
- Asaoka, S., Umehara, A., Otani, S., Fujii, N., Okuda, T., Nakai, S., Nishijima, W., Takeuchi, K., Shibata, H., Jadoon, W. A. & Hayakawa, S. 2018 Spatial distribution of hydrogen sulfide and sulfur species in coastal marine sediments Hiroshima Bay, Japan. *Marine Pollution Bulletin* **133**, 891–899. <https://doi.org/10.1016/j.marpolbul.2018.06.042>.
- Burduhos Nergis, D. D., Abdullah, M. M. A. B., Sandu, A. V. & Vizureanu, P. 2020 XRD and TG-DTA study of new alkali activated materials based on fly ash with sand and glass powder. *Materials* **13** (2), 343. <https://doi.org/10.3390/ma13020343>.
- Cara, C., Rombi, E., Mameli, V., Ardu, A., Sanna Angotzi, M., Niznansky, D., Musinu, A. & Cannas, C. 2018 γ -Fe₂O₃-M41S sorbents for H₂S removal: effect of different porous structures and silica wall thickness. *The Journal of Physical Chemistry C* **122** (23), 12231–12242. <https://doi.org/10.1021/acs.jpcc.8b01487>.
- Duan, P., Yan, C. & Zhou, W. 2017 Compressive strength and microstructure of fly ash based geopolymer blended with silica fume under thermal cycle. *Cement and Concrete Composites* **78**, 108–119. <https://doi.org/10.1016/j.cemconcomp.2017.01.009>.
- Eltarkawe, M. & Miller, S. 2019 Industrial odor source identification based on wind direction and social participation. *International Journal of Environmental Research and Public Health* **16** (7), 1242. <https://doi.org/10.3390/ijerph16071242>.
- Fajri, J. A., Fujisawa, T., Trianda, Y., Ishiguro, Y., Cui, G., Li, F. & Yamada, T. 2018 Effect of aeration rates on removals of organic carbon and nitrogen in small onsite wastewater treatment system (Johkasou). *MATEC Web of Conferences* **147**, 04008. <https://doi.org/10.1051/mateconf/201814704008>.

- Fuji, M. & Chikazawa, M. 2000 Reactivity to water and alcohol of siloxane formed by heat-treatment on silica powder surface. *Journal of the Society of Powder Technology, Japan* **37** (1), 19–25 (in Japanese with English abstract). <https://doi.org/10.4164/sptj.37.19>.
- Ichinari, T., Ohtsubo, A., Ozawa, T., Hasegawa, K., Teduka, K., Oguchi, T. & Kiso, Y. 2008 Wastewater treatment performance and sludge reduction properties of a household wastewater treatment system combined with an aerobic sludge digestion unit. *Process Biochemistry* **43** (7), 722–728. <https://doi.org/10.1016/j.procbio.2008.02.016>.
- Kamigawara, K. 2003 Odor regulation and odor measurement in Japan. In: *Odor Measurement Review*. Japan Ministry of the Environment, Tokyo, Japan, pp. 48–53.
- Khabazipour, M. & Anbia, M. 2019 Removal of hydrogen sulfide from gas streams using porous materials: a review. *Industrial & Engineering Chemistry Research* **58** (49), 22133–22164. <https://doi.org/10.1021/acs.iecr.9b03800>.
- Krach, K. R., Li, B., Burns, B. R., Mangus, J., Butler, H. G. & Cole, C. 2008 Bench and full-scale studies for odor control from lime stabilized biosolids: the effect of mixing on odor generation. *Bioresource Technology* **99** (14), 6446–6455. <https://doi.org/10.1016/j.biortech.2007.11.077>.
- Landmesser, H., Kosslick, H., Storek, W. & Fricke, R. 1997 Interior surface hydroxyl groups in ordered mesoporous silicates. *Solid State Ionics* **101** (1), 271–277. [https://doi.org/10.1016/S0167-2738\(97\)84042-8](https://doi.org/10.1016/S0167-2738(97)84042-8).
- Laskou, M., Margomenou-Leonidopoulou, G. & Balek, V. 2006 Thermal characterization of bauxite samples. *Journal of Thermal Analysis and Calorimetry* **84** (1), 141–146. <https://doi.org/10.1007/s10973-005-7126-5>.
- Liu, X. & Wang, R. 2017 Effective removal of hydrogen sulfide using 4A molecular sieve zeolite synthesized from attapulgite. *Journal of Hazardous Materials* **326**, 157–164. <https://doi.org/10.1016/j.jhazmat.2016.12.030>.
- Montes, D., Tocuyo, E., González, E., Rodríguez, D., Solano, R., Atencio, R., Ramos, M. A. & Moronta, A. 2013 Reactive H₂S chemisorption on mesoporous silica molecular sieve-supported CuO or ZnO. *Microporous and Mesoporous Materials* **168**, 111–120. <https://doi.org/10.1016/j.micromeso.2012.09.018>.
- Nassar, I. M., El-Din, M. R. N., Morsi, R. E., Abd El-Azeim, A. & Hashem, A. I. 2016 Eco friendly nanocomposite materials to scavenge hazard gas H₂S through fixed-bed reactor in petroleum application. *Renewable and Sustainable Energy Reviews* **65**, 101–112. <https://doi.org/10.1016/j.rser.2016.06.019>.
- Sado-Inamura, Y. & Fukushima, K. 2018 Considering water quality of urban rivers from the perspectives of unpleasant odor. *Sustainability* **10** (3), 650. <https://doi.org/10.3390/su10030650>.
- Selene, C. H. & Chou, J. 2003 *Hydrogen Sulfide: Human Health Aspects*. World Health Organization, Geneva, Switzerland, pp. 1–35.
- Su, Y.-M., Huang, C. Y., Chyou, Y.-P. & Svoboda, K. 2017 Sulfidation/ regeneration multi-cyclic testing of Fe₂O₃/Al₂O₃ sorbents for the high-temperature removal of hydrogen sulfide. *Journal of the Taiwan Institute of Chemical Engineers* **74**, 89–95. <https://doi.org/10.1016/j.jtice.2016.12.011>.
- Tran, D. T. 2016 Synthesis of porous ZnO based materials using an agarose gel template for H₂S desulfurization. *RSC Advances* **6** (2), 1339–1345. <https://doi.org/10.1039/C5RA21383E>.
- Wang, J., Yang, C., Zhao, Y.-R., Fan, H. L., Wang, Z. D., Shangguan, J. & Mi, J. 2017a Synthesis of porous cobalt oxide and its performance for H₂S removal at room temperature. *Industrial & Engineering Chemistry Research* **56** (44), 12621–12629. <https://doi.org/10.1021/acs.iecr.7b02934>.
- Wang, J., Wang, L., Fan, H., Wang, H., Hu, Y. & Wang, Z. 2017b Highly porous copper oxide sorbent for H₂S capture at ambient temperature. *Fuel* **209**, 329–338. <https://doi.org/10.1016/j.fuel.2017.08.003>.
- Wang, Y., Wang, Z., Pan, J. & Liu, Y. 2019 Removal of gaseous hydrogen sulfide using Fenton reagent in a spraying reactor. *Fuel* **239**, 70–75. <https://doi.org/10.1016/j.fuel.2018.10.143>.
- Wang, Y., Liu, X., Zhang, W., Li, Z., Zhang, Y., Li, Y. & Ren, Y. 2020 Effects of Si/Al ratio on the efflorescence and properties of fly ash based geopolymer. *Journal of Cleaner Production* **244**, 118852. <https://doi.org/10.1016/j.jclepro.2019.118852>.
- Wu, M., Jia, L., Fan, H. & Mi, J. 2017 Hot coal gas desulfurization using regenerable ZnO/MCM41 prepared via one-step hydrothermal synthesis. *Energy Fuels* **31** (9), 9814–9823. <https://doi.org/10.1021/acs.energyfuels.7b01615>.
- Yang, K., Su, B., Shi, L., Wang, H. & Cui, Q. 2018 Adsorption mechanism and regeneration performance of 13X for H₂S and SO₂. *Energy Fuels* **32** (12), 12742–12749. <https://doi.org/10.1021/acs.energyfuels.8b02978>.

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Supplemental materials

Removal of hydrogen sulfide gas using coal fly ash–blast furnace cement composite

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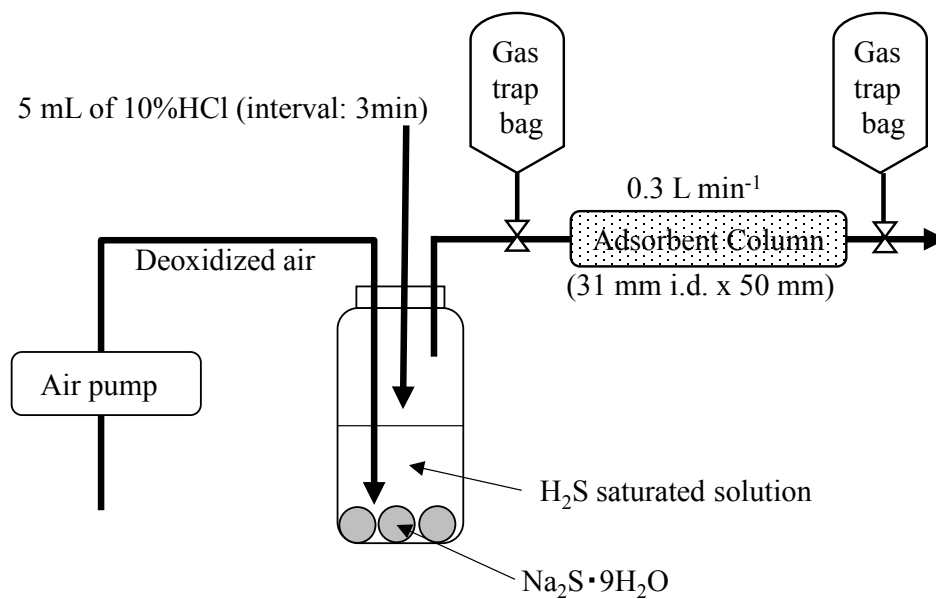


Fig. S1 Schematic of the removal experiments for hydrogen sulfide gas

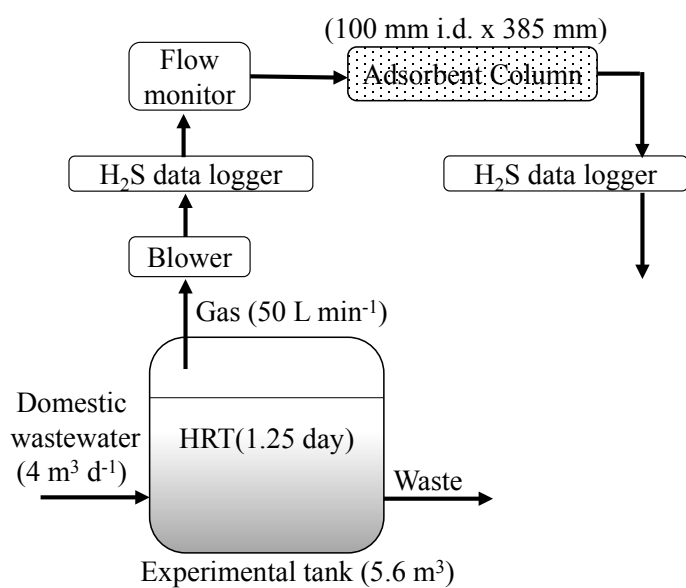


Fig. S2 Schematic of the pilot-scale experiment for removal of hydrogen sulfide gas derived from domestic wastewater

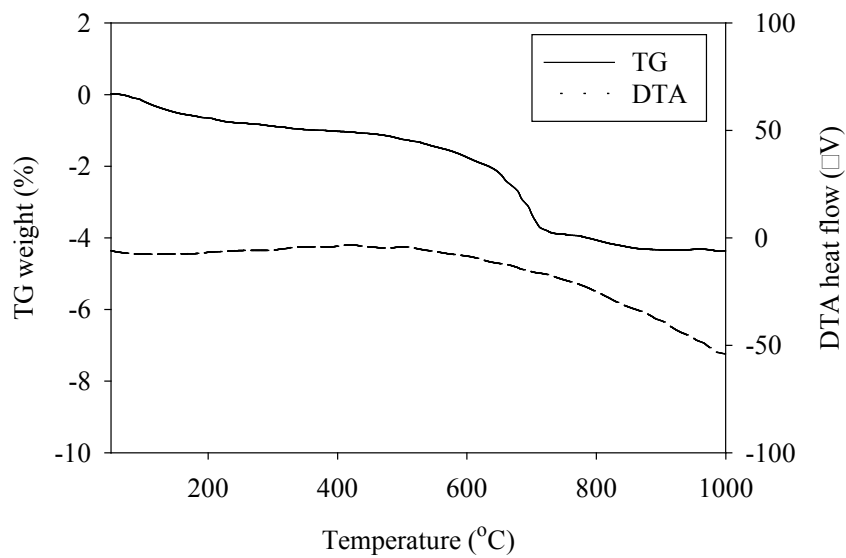


Fig. S3 Simultaneous thermogravimetry and differential thermal curves of the adsorbent

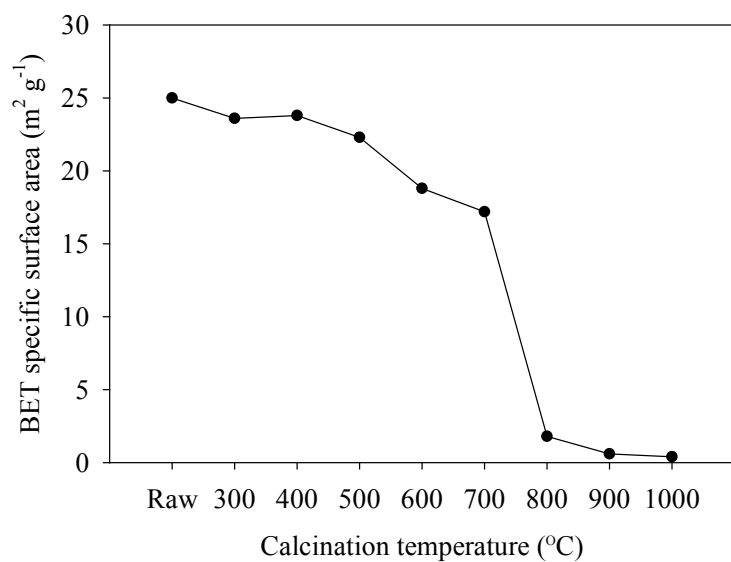


Fig. S4 Relationship between calcination temperature and BET surface area of the adsorbent

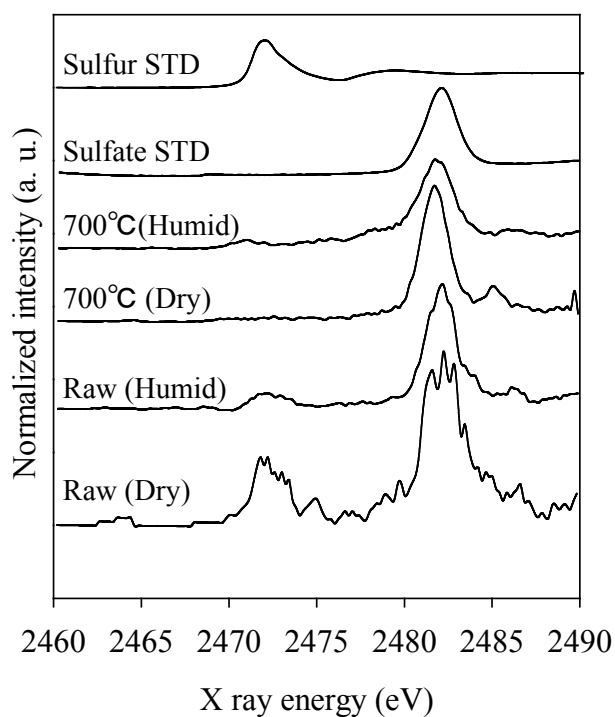


Fig. S5 Sulfur K edge spectra of adsorbents after adsorption of hydrogen sulfide gas and standards for sulfate and sulfur

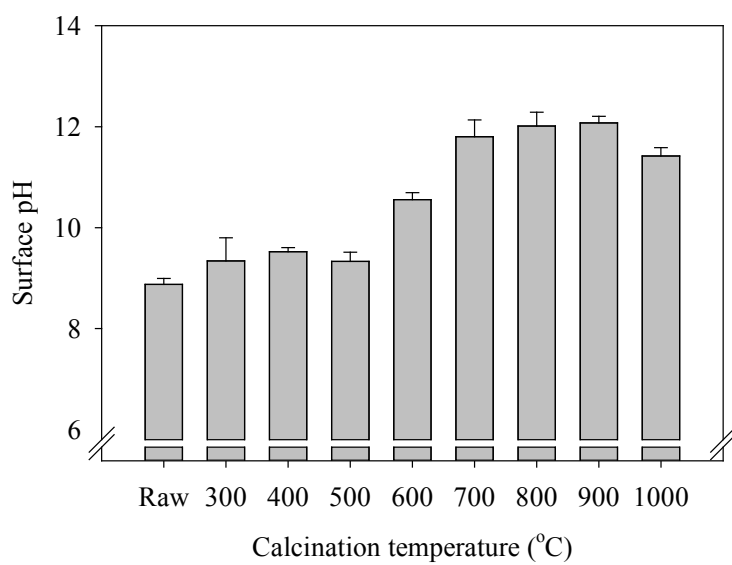


Fig. S6 Relationship between calcination temperature and surface pH of the adsorbent

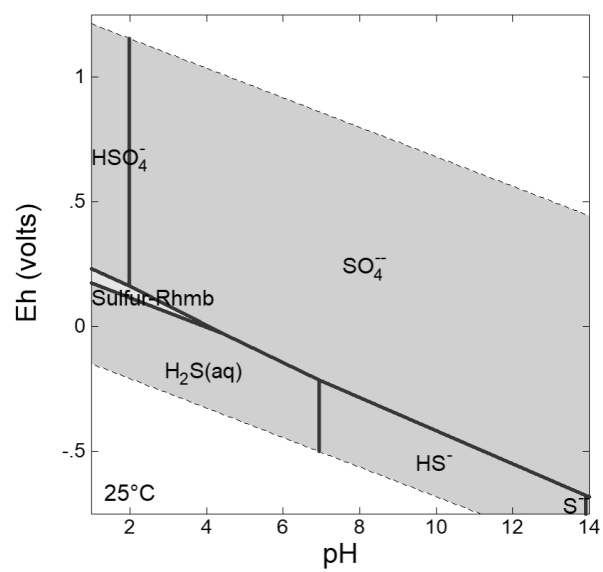


Fig. S7 Eh–pH diagram of sulfur