

Removal of Hydrogen Sulphide Gas Using Agricultural Wastes

T. Wajima

Abstract—In Japan, the total generation of biomass waste is 300 million tons annually, and the shortage of the final disposal site is a problem. Therefore, new use of agricultural waste is required. A representative gas for odor damage is hydrogen sulphide gas. In this study, removal capacity of agricultural wastes for low concentration hydrogen sulphide gas was examined to use as hydrogen sulphide gas adsorbent. Adsorption experiments on hydrogen sulphide gas (500 ppm) using peanut shell, rice straw, rice husk, and commercial charcoal were carried out. Experimental results showed that the adsorption amount of charcoal was 2335 mg/g, while those of agricultural wastes are very low (rice husk: 27 mg/g, peanut shell: 22 mg/g, rice straw: 18 mg/g). By pyrolyzing peanut shell, the H₂S gas adsorption of peanuts shell promote with increasing pyrolysis temperature due to the high specific surface area, and its adsorption amount of the product pyrolyzed at 600 °C is about 65% of charcoal.

Index Terms—Biomass waste, H₂S gas removal, pyrolysis, specific surface area.

I. INTRODUCTION

Hydrogen sulphide (H₂S) is a colorless flammable acid gas [1], which is produced mainly in the process of refineries, natural gas and biogas production. Its natural sources are volcanoes, natural gas wells and hot springs, and it can also be produced during the decomposition of bacteria. Because of its high toxicity, acidity and corrosiveness, it is very necessary to remove H₂S from industrial gas and oil streams [2]. The current common processes for H₂S removal include adsorption, absorption, catalytic oxidation and so on [3]-[7]. Wet desulfurization processes such as alcohol amine aqueous solution could be conducted normally under high sulphur load [8], [9]. However, the corrosion of equipment and pipelines resulting from the volatility of solvent (water) limited the wider application of conventional wet processes in the field of gas purification. In recent years, various industrial activities have caused serious pollution to the environment. Due to the low operating costs and high flexibility, adsorption is considered as one of the most effective technologies for pollutant management.

Agricultural waste is a great term for organic substances discharged by human beings in the process of agricultural production. Agricultural waste has loose and porous structures, and contains functional groups such as the carboxyl group, so it can be invoked as biological adsorption material. Agricultural waste gets the advantages of a wide range of sources, low cost, and renewable. It has a good prospect for the comprehensive utilization of resources when

used for environmental pollution control.

In recent years, a great deal of agricultural waste has been generated every year around the world. At present, extensive agricultural waste disposal methods not only fail to effectively convert and utilize agricultural resources, but also cause serious environmental pollution. A large amount of N₂O, SO₂, CH₄ and smoke are generated during the process of fecal burning and rice straw incineration, which seriously pollutes the atmosphere. Therefore, new utilization of agricultural waste without burning disposal are desired.

From these background, in this study, we attempted to use the agricultural waste as H₂S gas adsorbent.

II. EXPERIMENTAL

A. Materials

In this study, three agricultural wastes, peanuts shell, rice straw and rice husk, and commercially available charcoal (Wako) were used. Before using experiment, the samples were pulverized, sieved between 250 and 500 μm, and dried in a drying oven overnight. The properties of these samples were shown in Table I, which was analyzed using JIS M 8812 and JIS M 8819. Specific surface areas of samples are measured using BET measurement equipment (HM model-1210, Mountech), and surface morphologies are observed using scanning electron microscopy (JSM-6510, JEOL) equipped with energy dispersive X-ray spectroscopy (EDS). The photos and SEM images of three agricultural wastes are shown in Fig. 1 and Fig. 2, respectively.

TABLE I: THE PROPERTIES OF AGRICULTURAL WASTES AND CHARCOAL

	Specific surface area (m ² /g)	Moisture (%)	Ash (%)	Volatile matte and fixed carbon (%)		
				C	H	N
Peanuts shell	0.58	10.9	3.7	49.7	5.7	0.5
Rice straw	1.16	12.3	16.7	37.5	4.8	0.7
Rice husk	0.74	11.5	17.6	40.2	4.9	0.2
Charcoal	1451	12.0	6.7	> 90	-	-



Fig. 1. Photos of (a) peanuts shell, (b) rice straw and (c) rice husk.

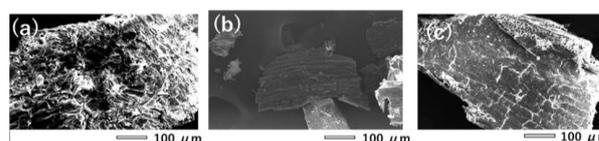


Fig. 2. SEM images of (a) peanuts shell, (b) rice straw and (c) rice husk.

Manuscript received January 19, 2020; revised March 30, 2020.

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B. H₂S Gas Removal Test

The experimental apparatus used in this study is shown in Fig. 3. The reactor was a fused silica tube (17 mm i.d., 1-m long), and was surrounded by an electric furnace to control its temperature. Sample (1 g) was set in the middle of quartz tube reactor sandwiched with sea sand (1 g) and glass wool. The reactor was purged with nitrogen gas at a flow rate of 100 mL/min for 30 min to remove oxygen, and then heated the reactor at 120 °C for 1 h to obtain the dried sample. After drying, the reactor was cooled to room temperature, and the flow of nitrogen gas stopped. The H₂S gas (500-ppmv H₂S in N₂) was fed at 100 mL/min into the reactor, and the H₂S concentration in the gas exiting the reactor was periodically measured using H₂S gas detector (GHS-8AT, GASTEC). In addition, peanuts shell was heated at 120, 200, 400, 600 and 800 °C in N₂ gas at drying process, and effect of pyrolysis on H₂S gas removal of agricultural waste was investigated. Mineralogical compositions of the samples are analysed using powder X-ray diffraction (XRD) (MiniFlex 600, Rigaku) and Fourier Transform Infrared (FT-IR) spectra are measured using FT-IR Spectroscopy (Nicolet iS5, Thermo Fisher Scientific).

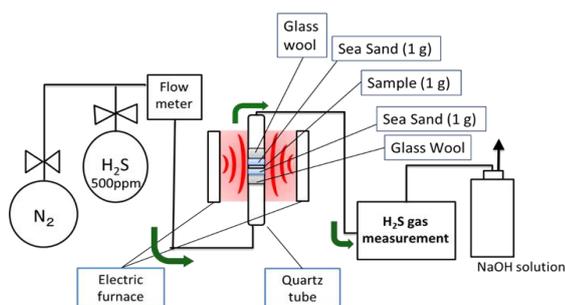


Fig. 3. Experimental apparatus.

III. RESULTS AND DISCUSSION

The H₂S concentration through the sample in the column is shown in Fig. 4. Three agricultural wastes indicate a little amount of H₂S removal, while charcoal remove H₂S gas clearly. The adsorption amounts of peanuts shell, rice straw, rice husk and charcoal are 22 mg/g, 18 mg/g, 27 mg/g and 2335 mg/g, respectively. It is noted that XRD patterns and FT-IR spectra of these samples after H₂S removal are almost same as those before removal.

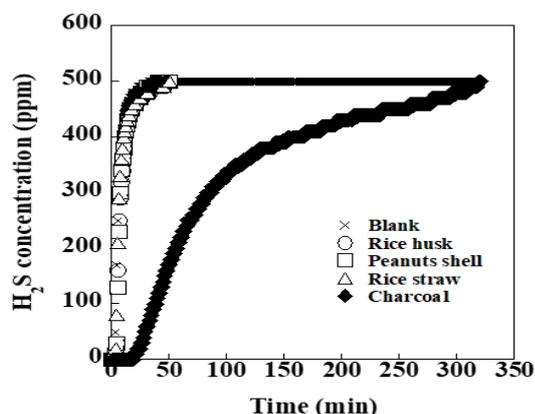


Fig. 4. H₂S gas concentration through the sample in column.

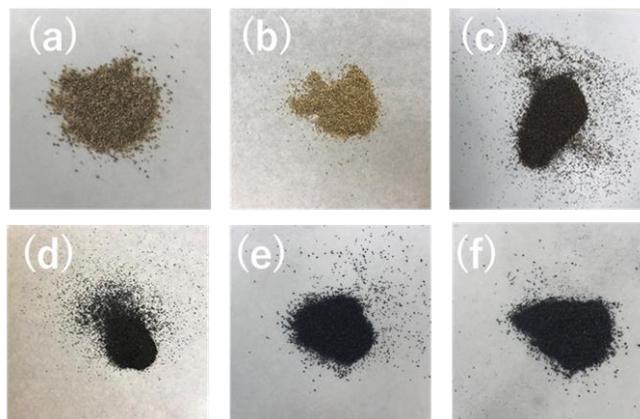


Fig. 5. Photos of (a) peanuts shell and the shell pyrolyzed at (b) 120 °C, (c) 200 °C, (d) 400 °C, (e) 600 °C and (f) 800 °C.

To improve the H₂S removal ability of agricultural wastes, agricultural waste, peanuts shell, was pyrolyzed to prepare carbonaceous material with high specific surface area. The photos of (a) peanuts shell and the shell pyrolyzed at (b) 120, (c) 200, (d) 400, (e) 600 and (f) 800 °C are shown in Fig. 5. Black powder, indicating carbonaceous material, can be obtained by pyrolyzing at more than 200 °C.

The XRD patterns of peanuts shell and the shell pyrolyzed at 120 °C, 200 °C, 400 °C, 600 °C and 800 °C are shown in Fig. 6. Raw sample and the sample pyrolyzed at 120 °C has cellulose structure, while amorphous material indicated by broad peaks without cellulose peaks can be obtained by pyrolyzing at more than 200 °C.

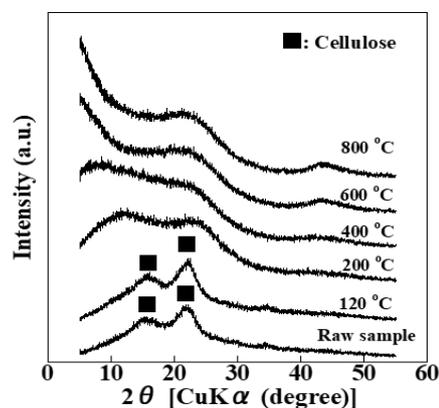


Fig. 6. XRD patterns of peanuts shell and the shell pyrolyzed at 120 °C, 200 °C, 400 °C, 600 °C and 800 °C.

SEM images of the peanuts shell pyrolyzed at (a) 200 °C, (b) 400 °C, (c) 600 °C and (d) 800 °C are shown in Fig. 7. The morphologies of the shell pyrolyzed at 200 – 600 °C are almost same, while that at 800 °C is different.

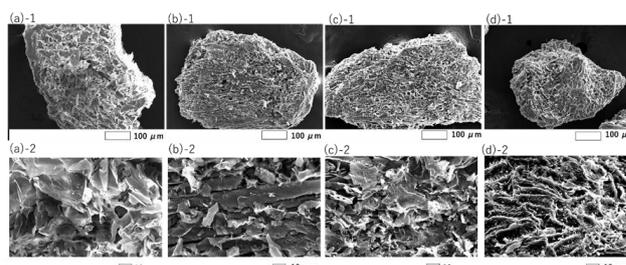


Fig. 7. SEM images of the peanuts shell pyrolyzed at (a) 200 °C, (b) 400 °C, (c) 600 °C and (d) 800 °C.

The H₂S concentration through the peanuts shell pyrolyzed at various temperatures in the column is shown in Fig. 8. With increasing the pyrolysis temperature of the peanuts shell, H₂S gas removal ability of the peanuts shell adsorbent increases.

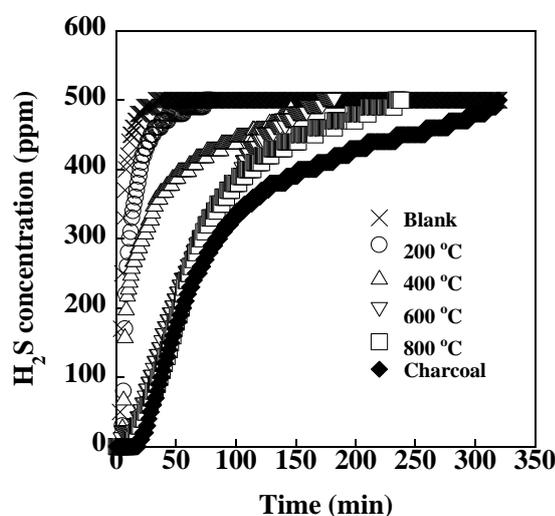


Fig. 8. H₂S gas concentration through the peanuts shell pyrolyzed at various temperatures in column.

The specific surface areas, H₂S adsorption amounts and sulphur contents of peanuts shell pyrolyzed at 200 - 800 °C after H₂S gas removal are shown in Table II. With increasing the pyrolysis temperature, specific surface area increases due to the surface morphology change, H₂S adsorption increases, and the sulphur content on the surface detected by EDS increases, indicating that H₂S adsorbed on the surface of the pyrolyzed shell increases.

TABLE II: THE SPECIFIC SURFACE AREAS, H₂S ADSORPTION AMOUNTS AND SULFUR CONTENTS OF PEANUTS SHELL PYROLYZED AT 200-800 °C AFTER H₂S GAS REMOVAL

	Specific surface area (m ² /g)	Adsorption amount (mg/g)	Sulphur content (%)
200 °C	0.62	195	0
400 °C	1.92	660	0.62
600 °C	92.3	1512	1.33
800 °C	239.4	1744	4.17

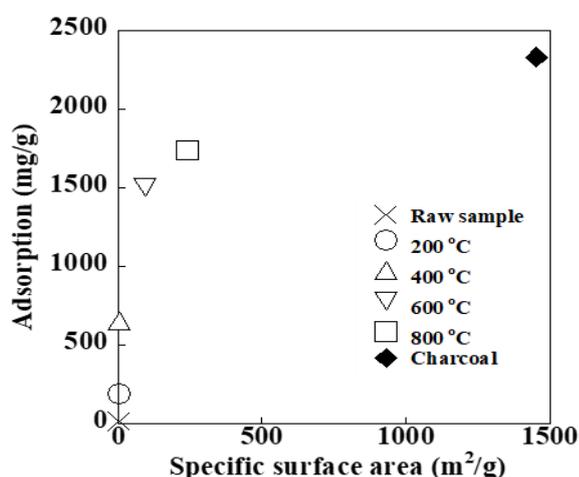


Fig. 9. The relationship between specific surface area and H₂S adsorption.

The relationship between specific surface area and H₂S adsorption is shown in Fig. 9. Raw peanuts shell has low specific surface area and low adsorption ability, and with increasing the pyrolysis temperature to 600 °C, both specific surface area and adsorption ability rapidly increase, and above 600 °C, adsorption amount are almost same regardless of specific surface area increase. The adsorption amount of the shell pyrolyzed at 600 °C is about 65 % of commercial charcoal while specific surface area is 20 %. Therefore, the agricultural waste with pyrolysis at 600 °C can be used for H₂S gas removal.

IV. CONCLUSION

For new utilization of waste agricultural wastes, H₂S gas removal behaviors of agricultural wastes, peanuts shell, rice straw and rice husk, was examined to be used as H₂S gas adsorbent. The H₂S gas adsorption abilities of agricultural wastes are very low (rice husk: 27 mg/g, peanut shell: 22 mg/g, rice straw: 18 mg/g), in comparison with commercial charcoal (2335 mg/g). The H₂S gas adsorption of peanuts shell was improved by pyrolysis, due to the promotion of specific surface area, and the adsorption amount of the shell pyrolyzed at 600 °C is about 65 % of commercial charcoal.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

T. Wajima conducted the research, analyzed the data, and wrote the paper. Author had approved the final version.

ACKNOWLEDGMENT

This work was partially supported by Hosokawa Powder Technology Foundation.

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