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Hung -Lung Chiang^a; Jiun -Horng Tsai^b; Chien -Liang Tsai^b; Yi -Chun Hsu^b

^a DEPARTMENT OF ENVIRONMENTAL ENGINEERING, FOOYIN INSTITUTE OF TECHNOLOGY, KAOSHSIUNG, TAIWAN, REPUBLIC OF CHINA ^b GRADUATE INSTITUTE OF ENVIRONMENTAL ENGINEERING, NATIONAL CHENG KUNG UNIVERSITY, TAINAN, TAIWAN, REPUBLIC OF CHINA

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Adsorption Characteristics of Alkaline Activated Carbon Exemplified by Water Vapor, H₂S, and CH₃SH Gas

HUNG-LUNG CHIANG*

DEPARTMENT OF ENVIRONMENTAL ENGINEERING
FOOYIN INSTITUTE OF TECHNOLOGY
KAOSHSIUNG, TAIWAN, REPUBLIC OF CHINA

JIUN-HORNG TSAI, CHIEN-LIANG TSAI, and YI-CHUN HSU

GRADUATE INSTITUTE OF ENVIRONMENTAL ENGINEERING
NATIONAL CHENG KUNG UNIVERSITY
TAINAN 70101, TAIWAN, REPUBLIC OF CHINA

ABSTRACT

Activated carbon adsorption is a widely used process in environmental engineering. Alkaline impregnated activated carbon has been used to enhance the adsorption capacity for odorous compounds from gas streams. This study investigated the physicochemical and adsorption characteristics of one virgin and four alkaline-impregnated activated carbon samples. The four alkaline additives were NaOH, Na₂CO₃, KOH, and K₂CO₃ and the impregnated activated carbons were referred to as NaOH-IAC, Na₂CO₃-IAC, KOH-IAC, and K₂CO₃-IAC. The specific surface area, micropore area, and micropore volumes were reduced in the impregnated activated carbon systems. The adsorption capacity of H₂S and CH₃SH increased. This indicated that the physical properties were not the predominant influence on adsorption behavior. The impregnated activated carbons were ranked NaOH > Na₂CO₃ > KOH > K₂CO₃ for H₂S adsorption. The NaOH-IAC demonstrated 3.2 and 2.2 times the adsorption capacity for H₂S and CH₃SH, respectively, compared to the virgin AC sample. Increasing the vacuum and immersion duration increased the alkaline quantity of NaOH impregnated on activated carbon. The NaOH-IAC₅₀ (50 mg NaOH/g carbon) sample performed the best. It had 6.9 times the adsorption capacity of the virgin AC. The humidity that coexisted in the H₂S and CH₃SH gas

* To whom correspondence should be addressed.

streams enhanced the H₂S and CH₃SH adsorption capacity of NaOH-IAC. At 50% relative humidity and 50 ppm H₂S, the NaOH-IAC sample exhibited the maximum adsorption capacity for H₂S. This carbon attained 30.3 times more capacity than the virgin AC.

Key Words. Hydrogen sulfide; Methyl mercaptan; Alkaline activated carbon; Humidity; Adsorption capacity; Principle component analysis

INTRODUCTION

The natural sources of sulfur that are emitted to the atmosphere are primarily reduced sulfur compounds such as dimethyl sulfide (C₂H₆S), dimethyl disulfide (C₂H₆S₂), hydrogen sulfide (H₂S), and methyl mercaptan (CH₃SH) rather than sulfur dioxide (SO₂) (1). Turk et al. (2) and Koe and Tan (3) reported the physical adsorption of such sulfur compounds on activated carbon. H₂S was usually removed from sour gas by absorption in an alkaline solution (4). Activated carbon has been used to remove H₂S and other odorous compounds from gas streams (5, 6). Alkaline-activated carbon, made by impregnating virgin AC with sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃) or sulfonated solutions, has successfully removed H₂S, CH₃SH, and trimethylamine [(CH₃)₃N] from gas mixtures with concentrations of 10 to 800 ppm (5). Impregnated activated carbon has also been used to remove ammonia (NH₃) and H₂S from a gas mixture (6). Furthermore, H₂S was efficiently removed from a sour gas with an alkaline-activated carbon (5-7).

When humidity is high, capillary condensation of water vapor takes place and the adsorption of solvents is hindered (8). Freeman et al. (14) indicated the adsorption of hydrogen cyanide (HCN) discouraged additional adsorption of water vapor. The adsorption of water vapor on activated carbon depends strongly on the concentrations of surface oxide groups and on the specific adsorption of water molecules in the micropore (9). Barton et al. (10) showed that the adsorption site initiating adsorption of water molecules on activated carbons are the CO-desorbing surface groups. Stoeckli et al. (11) suggested that the carbonyl-type groups are the primary adsorption centers for water molecules on various types of charcoal. Pore filling was possibly promoted by the presence of hydrophilic surface oxides (12).

The objectives of this study were: 1) to investigate which impregnated alkaline-activated carbon(s) increased adsorption capacity (including hydroxide and carbonate salts); 2) to determine the physicochemical characteristics of the impregnated activated carbons; 3) to determine the adsorption characteristics of a H₂S and CH₃SH mixture as gas systems; and 4) to determine the influence of water vapor on adsorption capacities.



EXPERIMENTAL

Preparation of Impregnated Activated Carbons

An activated carbon (RB₂; size: 2 mm, Norit Company, Netherlands) made from peat was used in this study. All solutions were prepared with analytical chemicals (Merck). A Mettler pH meter (Model 420A) was used for pH measurement. A strong acid (1 N HCl) and a base (1 N NaOH) were used for alkaline addition analysis. Unless otherwise noted, a strong acid [perchloric acid (0.1 M HClO₄)] and a strong base (0.2 M NaOH) were used for pH adjustments.

Fifty grams of the activated carbon were put into a stainless steel tube (15 mm in diameter, 35 cm in length). Nitrogen was added at 140°C for 6 hours to dewater and activate the activated carbon. Following the pretreatment process, each carbon was immersed in a 1 N NaOH, potassium hydroxide (KOH), Na₂CO₃, or potassium carbonate (K₂CO₃) solution for 4 hours. The slurry was then stirred for 30 minutes. After the carbon was vacuum processed for 30 minutes, it was filtered and dried in an oven at 130°C for 60 hours. The impregnated activated carbons were labeled NaOH-IAC, KOH-IAC, Na₂CO₃-IAC, and K₂CO₃-IAC, respectively. The nonimpregnated sample was identified as virgin AC.

Alkaline Addition Measurement

The alkaline content of NaOH, KOH, K₂CO₃, and Na₂CO₃ on each impregnated activated carbon was determined by titration. The carbon was placed in a vacuum oven (10⁻²–10⁻³ mmHg, 105°C) for 24 hours. Distilled water and a 1 N hydrochloric acid (HCl) solution were added to the impregnated carbon, and the slurry was shaken at 25°C for 24 hours. The supernatant was then titrated with a 1 N NaOH solution.

Physicochemical Characteristics Analysis

The physical characteristics of activated carbon, including specific surface area, micropore area, total pore volume, micropore volume, pore size distribution, and pore diameter, were measured by liquid N₂ adsorption at 77 K with an ASAP 2000 Micropore Analyzer.

An Element Analyzer (HERAEUS CHN-O Rapid Element Analyzer, USA) analyzed surface compositions of carbon, nitrogen, hydrogen, and oxygen. Acetanilide was used as the standard. Sulfur and chlorine were analyzed with a Tacussel Coulomax 78. Sulfanilic acid and 1-chloro-2,4-dintrobenzene were prepared as standards. Five samples were analyzed in duplicate.

Activated carbon samples were ground to a fine powder in an agate grinder. The mixture of KBr and the activated carbon powder was mixed in a weight



ratio of 300 to 1, then 150 mg of the mixture was weighed to prepare KBr pellets. The KBr pellets were stored in a desiccator until IR analysis. The IR spectrum was monitored over a frequency of 500 to 4000 cm^{-1} (Bohem, Model DA 3.002 FTIR).

Adsorption Process

The adsorption column was 8 cm long and 16 mm in diameter. The bottom of the column was packed with 3 cm of glass beads. The glass beads were used to assure adsorbates were mixed well. Activated carbon was packed in the adsorption column on top of the glass beads. Cylinder gas H_2S was blended with N_2 gas. A Sierra Mass Flowmeter (Series 9000) controlled the flow rate between 2.0 and 10 L/min. The concentrations of H_2S and CH_3SH ranged from 20 to 8000 ppm and 50 to 100 ppm, respectively, as analyzed by a Varian 3400 Gas Chromatograph/Flame Photometric Detector. The relative humidity of influent water vapor was between 0 to 80%. The capacity of the carbon to adsorb water vapor was weighed with a balance.

Principal Component Analysis

Influence factors in the H_2S , CH_3SH , and water vapor mixed gas adsorption system were examined by principle component analysis and performed by the Statistical Analysis System (SAS).

RESULTS AND DISCUSSIONS

Physicochemical Characteristics

Pore Characteristics

Table 1 shows the specific surface area, micropore area, micropore volume, and pore diameter of various activated carbons. The specific surface areas ranged from 683 to 931 m^2/g . The virgin AC had the largest surface area. The reduction ratio of the BET surface area was 18.6, 6.02, 11.4, and 26.6% for NaOH-IAC, Na_2CO_3 -IAC, KOH-IAC, and K_2CO_3 -IAC, respectively, compared to the virgin AC. Micropore area for the NaOH-IAC, Na_2CO_3 -IAC, KOH-IAC and K_2CO_3 -IAC impregnated activated carbons decreased from 646 to 529, 577, 518, and 397 m^2/g , respectively. This is a decrease of 18.1, 13.8, 19.8 and 38.5%, respectively, with respect to the virgin AC. The micropore volume for the impregnated activated carbon was also reduced, from 0.19 to 0.26 cm^3/g . When compared to the virgin AC 0.30 cm^3/g , the ratio decreased between 13.3 and 36.7%. The average pore diameters for the various activated carbon showed only a slightly variation between 15.57 and 15.73 \AA . Experimental results clearly indicated that the NaOH, Na_2CO_3 , KOH, and K_2CO_3 impregnated activated carbons decreased in specific surface area, micropore area, and micropore volume.



TABLE 1
Pore Characteristics of Alkaline Impregnated Activated Carbons and Their Adsorption Capacity for H_2S and CH_3SH Adsorption

Adsorbents	AC	NaOH-IAC	Na_2CO_3 -IAC	KOH-IAC	K_2CO_3 -IAC
Alkaline additive (mg/g)	—	23	25	20	39
BET surface area (m^2/g)	931	758	875	825	683
Micropore area (m^2/g)	646	529	557	518	397
Total pore volume (cm^3/g)	0.49	0.40	0.46	0.42	0.37
Micropore volume (cm^3/g)	0.30	0.25	0.26	0.25	0.19
Average pore diameter (\AA)	15.61	15.57	15.66	15.62	15.73
Adsorption capacity of H_2S (mg/g)	6.14	19.44	16.27	12.30	11.91
Adsorption capacity of CH_3SH (mg/g)	24.13	52.64	38.74	45.48	32.28

Although, the specific surface area, micropore area, and micropore volume of the impregnated activated carbons decreased, H_2S and CH_3SH adsorption increased. These phenomena demonstrate that physical properties were not the dominant adsorption capacity factors. The additive alkali was the significant factor. However, the four additives performed differently during H_2S and CH_3SH adsorption, and that can be attributed to the molecular size of the additives.

Elemental Compositions

Table 2 shows the results of elements on the activated carbon surface. The elemental compositions of C, H, and S on the activated carbon surface

TABLE 2
Element Composition of Alkaline Activated Carbons

Adsorbents	C (%)	H (%)	S (%)	N (%)	Cl (%)
AC	73.99	2.83	0.52	<0.01	<0.01
NaOH-IAC	71.17	2.28	0.28	<0.01	<0.01
Na_2CO_3 -IAC	74.55	1.76	<0.01	<0.01	<0.01
KOH-IAC	68.57	2.18	<0.01	<0.01	<0.01
K_2CO_3 -IAC	70.86	2.14	<0.01	<0.01	<0.01

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changed after alkaline treatment. Carbon contents were 73.99, 71.17, 74.55, 68.57, and 70.86% for AC, NaOH-IAC, Na₂CO₃-IAC, KOH-IAC, and K₂CO₃-IAC, respectively. The hydrogen content decreased from 2.83% for AC to 2.28, 1.76, 2.18, and 2.14% for NaOH-IAC, Na₂CO₃-IAC, KOH-IAC, and K₂CO₃-IAC, respectively. The sulfur content decreased from 0.52% (virgin AC) to 0.28% (NaOH-IAC), and was not detectable in the Na₂CO₃-IAC, KOH-IAC and K₂CO₃-IAC samples. An Element Analyzer did not detect nitrogen or chlorine on the activated carbon samples.

Impregnated activated carbon elements (C, H, and S) decreased after alkaline treatment. The alkaline may have extracted the elements from the activated carbon. However, there was no evidence that the change of elemental composition changed the H₂S and CH₃SH adsorption capacity.

Surface Functional Groups

Results of the activated carbon surface IR analysis are summarized in Table 3. The virgin AC aromatic ring, CH, and aromatic CH band positions were at 548–570, 699, and 759–776 cm⁻¹, respectively. The spectra of the alkaline-impregnated activated carbon showed no significant absorption peaks between 540 to 700 cm⁻¹. The absorption positions of the C—O band were 1125–1170 and 1208–1216 cm⁻¹. The absorption bands at 1383–1386 and 1456–1466 cm⁻¹ can be attributed to phenol. The aromatic C=C stretching

TABLE 3
Surface Functional Groups of the Activated Carbons by IR Analysis

Functional groups	Absorption peaks (cm ⁻¹)				
	AC	NaOH-IAC	KOH-IAC	Na ₂ CO ₃ -IAC	K ₂ CO ₃ -IAC
Aromatic ring	548	—	—	570	—
C—H	699	—	—	—	—
C—H ^a	776	759	—	—	—
C—O stretch and vibration	—	1170	—	1170	1125
C—O or phenoxy absorption	1208	1216	1212	—	—
Phenol	1384	1384	1383	1386	1386
	—	1466	—	1456	—
C=O stretch, carboxyl	1571	1565	1568	1567	1570
C=O ^b	—	1738	—	—	—
Aliphatic CH ₂ and CH ₃	2922	2923	2920	2923	2922
—OH	3441	3434	3470	3345	3508

^a With ring vibration.

^b Unsaturated δ-lactone.



vibration peaks were observed at 1571 cm^{-1} of the AC as well as at 1565 cm^{-1} for NaOH-IAC, 1568 cm^{-1} for KOH-IAC, 1567 cm^{-1} for Na_2CO_3 -IAC, and 1570 cm^{-1} for K_2CO_3 -IAC. There was a weaker band in the carboxylic acid $\text{C}=\text{O}$ region at 1738 cm^{-1} for NaOH-IAC. A strong and broad OH region band at $3345\text{--}3508\text{ cm}^{-1}$ was shown for all activated carbon samples. The spectra of CH_3 and CH_2 stretch were at $2920\text{--}2923\text{ cm}^{-1}$. However, the weak band at 1738 cm^{-1} in the sodium salt of activated carbon may have been due to a normal carbonyl group. The activated carbon spectra revealed a chemical shift that was due to the reaction of alkaline with activated carbon.

Alkaline Impregnation

Table 1 also shows the alkaline impregnation ratios on activated carbons. The alkaline additives impregnated on virgin AC ranged from 0.18 to 0.58 mmol/g and were ranked $\text{NaOH} > \text{Na}_2\text{CO}_3 > \text{KOH} > \text{K}_2\text{CO}_3$. The moles of NaOH impregnated on the virgin AC were 1.6–3.2 times greater than the other impregnation solutions. The molecular size of NaOH is smaller than Na_2CO_3 , KOH, or K_2CO_3 , which implies that it is easier to transport into the activated carbon pores, thus making it the best impregnating additive on carbon.

H_2S and CH_3SH Adsorption Capacity of Alkaline Activated Carbons

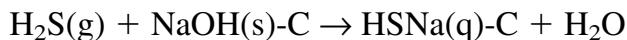
When the H_2S loading in the influent stream was 1.08 mg/min (250 ppmv , 3.1 L/min at 25°C), the H_2S adsorption capacity on the impregnated adsorbents was 19.44 mg/g (NaOH-IAC), 16.27 mg/g (Na_2CO_3 -IAC), 12.30 mg/g (KOH-IAC), 11.91 mg/g (K_2CO_3 -IAC), and 6.14 mg/g (AC). The results are summarized in Table 1. The H_2S adsorption capacity for NaOH-IAC was 3.2 times that of the virgin AC. When the influent concentration of CH_3SH was 1.96 mg/min (100 ppmv , 10 L/min at 25°C) the CH_3SH adsorption capacities on AC, NaOH-IAC, Na_2CO_3 -IAC, KOH-IAC, and K_2CO_3 -IAC were 24.14 , 52.64 , 38.74 , 45.48 , and 32.28 mg/g , respectively. NaOH-IAC had the maximum adsorption capacity (up to 2.2 times the virgin AC). It was selected as the test system for the series experiments.

H_2S and CH_3SH adsorption capacities were enhanced with NaOH-IAC; more NaOH was impregnated on the activated carbons than the other alkalines. Molecularly, NaOH is smaller than KOH, which is smaller than Na_2CO_3 and K_2CO_3 . NaOH was impregnated on the activated carbons in a 0.575 mmol/g ratio while KOH, K_2CO_3 , and Na_2CO_3 were absorbed in 0.357 , 0.282 , and 0.236 mmol/g ratios, respectively (Table 1). The smaller molecules were transported into the small pores of the activated carbon more easily and, therefore, produced higher adsorptive capacities. Conceptually, the enhanced adsorption capacity reaction system can be explained by two mechanisms: the



H_2S mixture gas with or without water vapor. CH_3SH can be substituted in the following NaOH-IAC examples.

(1) Without Water Vapor Reaction. H_2S was transported to the surface of the alkaline activated carbon and then reacted (adsorbed) with the NaOH. The H_2S adsorbed on solid surface and generated two products and a water film on the surface of alkaline activated carbon.



and

(1)



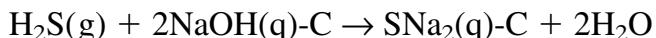
where $\text{H}_2\text{S(g)}$ is H_2S gas without water vapor. NaOH(s)-C is NaOH impregnated on the activated carbon. HSNa(q)-C , and $\text{SNa}_2\text{(q)-C}$ are the compounds formed on the activated carbon and covered by a water film.

Following Eq. (1), the impregnated activated carbon would be covered by the generated H_2O . H_2S would then react with the water film (absorption and acid-base reaction) as follow:



and

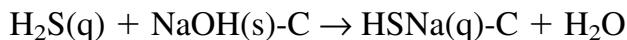
(2)



where NaOH(q)-C is the NaOH impregnated on the activated carbon covered by the water film.

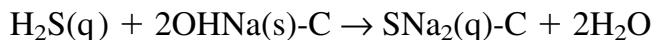
(2) With Water Vapor Reaction. The adsorption of H_2S on the impregnated activated carbon could proceed in two directions depending on whether the mixture of H_2S gas water vapor had reacted or not before activated carbon impregnation.

First, if the H_2S was previously absorbed by (dissolved into) water vapor, the reactions follows Eq. (3):



and

(3)



where $\text{H}_2\text{S(q)}$ is H_2S gas dissolved in water vapor.

Second, if the H_2S had not been previously dissolved in the water vapor mixture, the reaction would follow Eq. (2). Because alkaline (NaOH) easily absorbs water vapor, a water film will form on the surface of alkaline-activated carbon (Table 5). Since the H_2S and water vapor mixture showed much greater H_2S adsorption ability (Table 6), the H_2S was transported into and reacted with the water film (absorption and acid-base reaction). Equation (2) would be the dominant reaction mechanism.



TABLE 4
NaOH Impregnated on Activated Carbon under Various Preparation Conditions

Stir time (min)	Vacuum time (min)	Stationary time (min)	Impregnated dosage (mg/g)	Adsorption of H ₂ S (mg/g)
30	20	190	23	19.4
30	30	200	50	43.5
30	40	210	65	33.3
30	40	230	70	29.3

NaOH Impregnated on Activated Carbon

The amount of NaOH impregnated on activated carbon depends on the impregnation procedure. The NaOH concentrations impregnated on carbon under diverse conditions of vacuum and immersion duration are shown in Table 4. Increasing the vacuum and immersion duration increased the alkaline concentration of the NaOH-impregnated activated carbons.

The H₂S adsorption capacity of impregnated NaOH-IAC is shown in Table 4. With a H₂S flow rate of 1.08 mg/min (250 ppmv, 3.1 L/min at 25°C), the adsorption capacity of NaOH-IAC₅₀ (50 mg NaOH impregnated on 1 g virgin AC) was 43.5 mg/g while NaOH-IAC₆₅, NaOH-IAC₇₀, and NaOH-IAC₂₃ capacities were 33.3, 29.3, and 19.4 mg/g, respectively. Increasing NaOH impregnation on virgin AC did not ensure increased adsorption capacity.

Experimental results indicate that NaOH-IAC₅₀ had the maximum adsorption H₂S capacity among the four preparative conditions, thus making it the optimal concentration. NaOH concentrations greater than 50 mg/g may have plugged the activated carbon micropores and reduced the effective area for adsorption. Furthermore, the NaOH may have crystallized during the drying procedure, which would result in less effective adsorption. Smaller NaOH additions, however, were less effective on adsorption capacity than the NaOH-IAC₅₀.

Adsorption Characteristics of Humidified Gas

Adsorption of Water Vapor

The water vapor adsorption capacities for AC and NaOH-IAC are shown in Table 5. The relative humidity (RH) of influent gas increased from 20 to 80%. The adsorption capacity of water vapor improved from 6 to 321 mg/g for virgin AC and from 258 to 334 mg/g for NaOH-IAC. The cross-section area of water is 12.5 Å² (13); the percentage of AC surface coverage was from 2.70



TABLE 5
Adsorption Capacity of Water Vapor for AC and NaOH-IAC

Adsorbent ^a		Relative humidity (%)				
		80	65	50	30	20
AC	Adsorption capacity of H ₂ O ¹ (mg/g)	321	318	14	8	6
	Adsorption capacity of H ₂ O (mmol/g)	17.8	17.7	0.8	0.4	0.3
	Surface area of adsorbate ^b (m ²)	1340.8	1330.3	59.4	33.4	25.1
	Percentage of surface coverage (%)	144	143	6.4	3.6	2.7
NaOH-IAC	Adsorption capacity of H ₂ O (mg/g)	334	329	296	290	258
	Adsorption capacity of H ₂ O (mmol/g)	18.6	18.3	16.4	16.1	14.3
	Surface area of adsorbate (m ²)	1398.3	1377.4	1237.4	1213.5	1078.0
	Percentage of surface coverage (%)	186	182	163	160	142

^a The BET surface areas of AC and NaOH-IAC are 931 and 758 m²/g, respectively.

^b The cross-sectional area of H₂O is 12.5 Å² (13).

to 144% for relative humidity between 20 and 80%. The percentage of NaOH-IAC surface coverage was from 142 to 184% for relative humidity between 20 and 80%. The adsorption capacity of water vapor for AC and NaOH-IAC is obviously different at a relative humidity less than 60% and is similar at a relative humidity greater than 60%.

Two distinct adsorption sites for virgin AC are postulated to account for the small amount of adsorption followed by the rapid rise. Initially, surface oxides in the micropores act as adsorption centers and permit adsorption by the formation of hydrogen bonds between the water molecules and surface oxides. The adsorbed water molecules act as secondary adsorption sites that can retain other water molecules by means of hydrogen bonds. As the number of secondary adsorption sites increases, the rapid adsorption increases between 40 and 60% RH. This is due to the increasing probability of adsorption followed by the eventual coalescence of these complexes (14, 15). The NaOH-impregnated activated carbon could increase the activated carbon surface oxides or the NaOH could absorb water vapor more easily. NaOH-IAC could therefore adsorb more water vapor at a lower relative humidity.



Adsorption Capacity of H₂S in Humidified Gas

Table 6 shows the adsorption capacity of water vapor and H₂S mixed gas on NaOH-IAC. With an influent flow of 100 ppm H₂S and relative humidities of 50 and 80%, the H₂S adsorption capacities were 151 and 79 mg/g. The water vapor adsorption capacities were 204 and 248 mg/g, respectively. When the H₂S concentration in the influent concentration was 50 ppm and the relative humidities were 50 and 80%, the H₂S adsorption capacities were 186 and 142 mg/g, and the water vapor adsorption capacities were 166 and 205 mg/g, respectively. Obviously, water vapor was beneficial in the mixed gas. The vapor easily adsorbed on the NaOH-IAC and formed a film on the surface of NaOH-IAC. Then the H₂S reacted with the basic surface of NaOH-IAC.

Experimental results indicated that the adsorption capacities of H₂S and water vapor on NaOH-IAC were much greater than on virgin AC. When water vapor was added to the H₂S gas stream, the H₂S adsorption capacity of NaOH-IAC was 2.6–6.9 times the value at the dry H₂S gas stream condition. This enhancement has been shown in other results (9–11). Water vapor and H₂S mixed gas may transfer to the IAC by adsorption and adsorption, but adsorption is the predominant mechanism between H₂S and NaOH-IAC.

We used a cross-sectional area of adsorption to measure the coverage of activated carbon. Results indicated that two molecular layers covered the activated carbon at a relative humidity higher than 50%. Without water vapor, the

TABLE 6
Adsorption Capacity of Water Vapor and H₂S Mixture Gas on NaOH-IAC

	Relative humidity (%)						
	0		50		80		
Concentration (ppm)	30	50	100	50	100	50	100
Adsorption capacity of H ₂ S ^a (mg/g or mmol/g)	25 (0.74) ^b	27 (0.80)	31 (0.92)	186 (5.47)	151 (4.45)	142 (4.17)	79 (2.31)
Adsorption capacity of H ₂ O ^a (mg/g or mmole/g)	—	—	—	166 (9.23)	204 (11.34)	205 (11.38)	248 (13.80)
Surface area of H ₂ S (m ² /g)	112	120	138	822	669	627	347
Surface area of H ₂ O (m ² /g)	—	—	—	694	853	857	1037
Percentage of surface coverage (%) ^c	14.8	15.9	18.3	200	201	183	196

^a Molecular cross-sectional areas of H₂S and H₂O are 25 and 12.5 Å² (13).

^b Adsorption capacity of H₂S and H₂O (mmol/g).

^c Total surface area = (surface area of H₂S) + (surface area of H₂O). The surface area of NaOH-IAC is 758 m²/g.



TABLE 7
Adsorption Capacity of Water Vapor, H₂S, and CH₃SH Mixture Gas on NaOH-IAC

Concentration ratio	Relative humidity (%)								
	0			50			80		
	1/1	2/1	1/2	1/1	2/1	1/2	1/1	2/1	1/2
Adsorption capacity of H ₂ S (mg/g or mmol/g)	29 (0.86) ^a	49 (1.44)	10 (0.40)	27 (0.79)	64 (1.87)	60 (1.76)	38 (1.13)	33 (0.97)	60 (1.77)
Adsorption capacity of CH ₃ SH (mg/g or mmol/g)	48 (1.00)	30 (0.62)	58 (1.22)	11 (0.24)	81 (1.68)	22 (0.45)	25 (0.52)	21 (0.44)	49 (1.03)
Adsorption capacity of H ₂ O (mg/g or mmol/g)	—	—	—	292	219	275	301	323	285
Surface area of H ₂ S (m ² /g)	129	212	46	119 (16.22)	282 (12.18)	265 (15.27)	169 (16.74)	147 (17.95)	266 (15.86)
Surface area of CH ₃ SH (m ² /g)	211	129	255	50	353	95	110	92	216
Surface area of H ₂ O (m ² /g)	—	—	—	1220	917	1149	1260	1351	1193
Percentage of surface coverage (%) ^c	45	46	40	183	205	199	203	221	210

^a Adsorption capacity of H₂S, CH₃SH, and H₂O (mmol/g).

^b Molecular cross-sectional areas of H₂S, CH₃SH, and H₂O are 25, 34.8, and 12.5 Å² (13).

^c Total surface area = (surface area of H₂S) + (surface area of H₂O). The surface area of NaOH-IAC is 758 m²/g.

H₂S adsorption capacity was less than 18.3%, while with water vapor the capacity was greater than 183% (Table 6). That showed that water vapor was easily adsorbed on the surface of NaOH-treated activated carbon.

Adsorption Capacity of H₂S and CH₃SH in Humidified Gas

Table 7 shows the adsorption results of a H₂S, CH₃SH, and water vapor mixed gas system. The surface coverage was between 40 and 45% in the H₂S and CH₃SH mixed gas system without water vapor. When the influent concentration ratios of H₂S and CH₃SH were 1/1, 2/1, and 1/2 (100/100 ppm, 100/50 ppm, and 50/100 ppm), the corresponding adsorption capacities of H₂S and CH₃SH were from 0.30 to 1.44 mmol/g and 0.62 to 1.22 mmol/g, respectively.

In the water vapor mixed gas system the adsorption capacity of H₂S increased to between 0.79 and 1.87 mmol/g while the CH₃SH adsorption capacity increased to between 0.24 to 1.68 mmol/g. The adsorption capacity of water vapor was between 12.18 to 17.95 mmol/g for the H₂S and CH₃SH. The percentage of surface coverage was a nearly constant 203 ± 12.5%. The re-



sults again indicate that water vapor is advantageous for adsorption in the H_2S , CH_3SH , and water vapor mixture gas system.

Factors Affecting the Adsorption of Odor Gas

Tables 8 and 9 shows the principal component analysis results for operation factors and surface coverage on odorous gas adsorption. The results for the H_2S and water vapor adsorption mix show that Group I factors are important. These included relative humidity (RH), adsorption capacity of H_2S (AC- H_2S), adsorption capacity of H_2O (AC- H_2O), surface coverage (SC), and the mole of total adsorption capacity (MTAC). Group II factors are important in H_2S ($\text{C}-\text{H}_2\text{S}$) concentration. The percentages of total variance as explained by Groups I and II were 78.6 and 16.2, respectively. The results of Group II analysis indicated that AC- H_2S could influence the H_2S and water vapor mixture gas adsorption system.

Results of the principle component analysis show that four factors could affect the adsorption system of the H_2S , CH_3SH , and water vapor mixture gas. The major parameters of Factor I were RH, AC- H_2O , SC, and MAC, and the minor parameter was AC- H_2S . The major parameter of Factor II analysis was AC- CH_3SH , and the minor parameters were CR and AC- H_2S . The major parameter of Factor III was CR. The minor parameter of Factor IV was AC- H_2S . Based on Factor I, the results imply that RH, AC- H_2O , SC and MAC could affect the H_2S , CH_3SH , and water vapor adsorption system.

According to the results of the principle component analysis, the relative humidity, AC- H_2O , SC, and MAC are important in both H_2S and water vapor, and the H_2S , CH_3SH , and water vapor mixture gas adsorptions are important on alkaline-activated carbon samples.

TABLE 8
Results of Principal Components Analysis among Operation Factors, Surface Coverage, and Adsorption Capacities: Water Vapor and H_2S Adsorption

Items	Factor I	Factor II
Relative humidity, RH (%)	0.951	0.029
Concentration, C (ppm)	0.330	-0.933
Adsorption capacity of H_2S , AC- H_2S (mg/g)	0.862	0.307
Adsorption capacity of H_2O , AC- H_2O (mg/g)	0.985	-0.059
Surface coverage, SC (%)	0.995	0.045
Mole of adsorption capacity, MAC (mmol/g)	0.999	0.030
Variance explained	4.713	0.972
Percentage of total variance explained	78.55	16.19
Major parameters	RH, AC- H_2S , AC- H_2O , SC, MAC	C



TABLE 9
Results of Principal Components Analysis among Operation Factors, Surface Coverage, and Adsorption Capacities: Water Vapor, H₂S, and CH₃SH Adsorption^a

Items	Factor I	Factor II	Factor III	Factor IV
Relative humidity, RH (%)	0.966	-0.041	0.020	0.162
Concentration, CR	0.025	0.574	-0.812	0.100
Adsorption capacity of H ₂ S, AC-H ₂ S (mg/g)	0.536	0.646	0.195	-0.507
Adsorption capacity of CH ₃ SH, AC-CH ₃ SH (mg/g)	-0.313	0.740	0.457	0.381
Adsorption capacity of H ₂ O, AC-H ₂ O (mg/g)	0.987	-0.125	-0.015	0.078
Surface coverage, SC (%)	0.989	0.074	0.030	0.090
Mole of adsorption capacity, MAC (mmol/g)	0.995	-0.039	0.025	0.067
Variance explained	4.261	1.319	0.908	0.457
Percentage of total variance explained	60.87	18.84	12.98	6.53
Major parameters	RH, AC-H ₂ O, SC, MAC	AC-CH ₃ SH	CR	—
Minor parameters	AC-H ₂ S	CR, AC-H ₂ S	—	AC-H ₂ S

^a Major factor is the factor loading higher than 0.7. Minor factor is the factor loading between 0.5 and 0.7.

CONCLUSIONS

Although specific surface area and pore volumes decreased by nearly 20% on NaOH-IAC, the adsorption capacity of H₂S was enhanced 3.2 times, which indicates that physical characteristics were not the predominant influence in the H₂S adsorption capacity of NaOH-IAC. In addition, the element composition and function groups on the surface of NaOH-IAC were obviously different from those on AC. The NaOH-IAC adsorption capacity for H₂S and water vapor is greater than that of virgin AC. When water vapor was present in the gas stream, the NaOH-IAC adsorption capacity for H₂S increased. The results indicate NaOH-impregnated activated carbon (NaOH-IAC) adsorbs H₂S and water vapor better than virgin AC.

NOMENCLATURE

AC activated carbon
IAC impregnated activated carbon



NaOH-, KOH-, Na_2CO_3^- , or K_2CO_3 -IAC	NaOH-, KOH-, Na_2CO_3^- , or K_2CO_3 -impregnated activated carbon
NaOH-IAC ₅₀	50 mg NaOH impregnated on 1 g virgin AC
RH	relative humidity (%)
C	concentration (ppm)
CR	concentration ratio
AC-H ₂ S	adsorption capacity of H ₂ S (mg/g)
AC-CH ₃ SH	adsorption capacity of CH ₃ SH (mg/g)
AC-H ₂ O	adsorption capacity of H ₂ O (mg/g)
SC	surface coverage (%)
MAC	mole of adsorption capacity (mmol/g)
I, II, III, IV	factors

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REFERENCES

1. C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, "Kinetics and Mechanisms of the Reactions of CH₃SH Radical with O₂, NO, and NO₂," *J. Phys. Chem.*, **96**, 696–701 (1992).
2. A. Turk, E. Sakalis, J. Lessuck, H. Karamitsos, and O. Rago, "Ammonia Injection Enhances Capacity of Activated Carbon for Hydrogen Sulfide and Methyl mercaptan," *Environ. Sci. Technol.*, **23**, 1242–1245 (1989).
3. L. C. C. Koe and N. C. Tan, "Comparison of Field and Laboratory H₂S Adsorption Capacity of Activated Carbon," *Water Air Soil Pollut.*, **50**, 969–976 (1990).
4. P. A. Ferguson, *Hydrogen Sulfide Removal from Gases, Air and Liquids*. Noyes Data Corporation, New Jersey, 1975.
5. H. Ikeda, H. Asaba, and Y. Takeuchi, "Removal of H₂S, CH₃SH and (CH₃)₃N from Air by Use of Chemically Treated Activated Carbon," *J. Chem. Eng. Jpn.*, **21**, 91–97 (1988).
6. J. H. Tsai, F. T. Jeng, and S. H. Yen, "Treatment of NH₃ and H₂S Mixture Gas by Sorption," *J. Chin. Inst. Environ. Eng.*, **22**, 211–218 (1992).
7. S. Tsutsui and S. Tanada, "Adsorption of Hydrogen Sulfide, Dimethyl Sulfide and Their Binary Mixture into Pores of N-containing Activated Carbon," *Chem. Pharm. Bull.*, **35**, 1238–1242 (1987).



8. M. Okazaki, H. Tamon, and R. Toei, "Prediction of Binary Adsorption Equilibria of Solvent and Water Vapor on Activated Carbon," *J. Chem. Eng. Jpn.*, **11**, 209–215 (1978).
9. L. A. Jonas and J. A. Rehrmann, "The Kinetics of Adsorption of Organophosphous Vapors from Mixtures by Activated Carbon," *Carbon*, **10**, 657–663 (1972).
10. S. S. Barton, M. J. B. Evans, and B. H. Harrison, "Surface Studies on Carbon: Water Adsorption on Polyvinylidene Chloride Carbon," *J. Colloid. Interface Sci.*, **45**, 542–548 (1973).
11. H. F. Stoeckli, F. Krahenbuel, and D. Morel, "The Adsorption of Water by Active Carbons in Relation to the Enthalpy of Immersion," *Carbon*, **21**, 589–591 (1983).
12. R. Doborwolski, M. Jaroniec, and A. Swiatkowski, "Adsorption of Water Vapor on Modified Activated Carbons," *Monatsh. Chem.* **121**, 971–978 (1990).
13. A. E. McClellan and H. F. Harnsberger, "Cross-sectional Areas of Molecules Adsorbed on Solid Surfaces," *J. Colloid Interface Sci.*, **23**, 577–599 (1967).
14. G. B. Freeman and P. J. Reucroft, "Adsorption of HCN and H₂O Vapor Mixtures by Activated and Impregnated Carbons," *Carbon*, **16**, 313–316 (1978).
15. M. M. Dubinin, "Water Vapor Adsorption and the Microporous Structure of Carbonaceous Adsorbents," *Carbon*, **18**, 355–364 (1980).

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