Increasing Adsorption Efficiency of Activated Carbon for H_2S Removal by Surface Oxidation and Metal Addition

สมเกียรติ กรวยสวัสดิ์*

Abstract

The present investigation was undertaken to study the method of improving the adsorption capacity of activated carbon for H_2S by surface oxidation and metal addition techniques. The coconut shell-based activated carbon samples were pretreated with O_3 and HNO_3 oxidants. The oxidation techniques were used to introduce the functional groups such as C-O and/or C=O on the surface of activated carbon samples. These include, for example, hydroxyl, ketone, carboxylic acid, and ether structures and their existence were ascertained by FT-IR spectroscopy. Zinc acetate [$Zn(C_2H_3O_2)_2$] was used as an impregnant for the metal addition step after the carbon samples were oxidized with O_3 or HNO_3. A synthetic gas mixture of 1.01wt % H_2S plus balance N_2 was used for the fixed-bed adsorption experiments. The outlet concentration of H_2S from the fixed-bed adsorber was followed as a function of time by an electrochemical sensor. Adsorption capacity (mg H_2S adsorbed/g adsorbent) up to the breakthrough time was used to assess the efficiency of H_2S removal. Zn-impregnated samples gave higher adsorption capacity than the single-step oxidized samples and an untreated samples at temperatures of 10, 30 and 45°C. The carbon sample treated with 6.0 M HNO_3 and Zn impregnation gave the highest adsorption capacity for H_2S, giving increased adsorption efficiency of 230% over that of the untreated sample at 45°C. The maximum increase of 180% adsorption efficiency over that of untreated sample was observed for the O_3 oxidized sample impregnated with Zn. There was a tendency that the chemical adsorption of H_2S increased with the amount of Zn impregnated on the surface sample at temperatures of adsorption higher than 45°C, indicating the significant role of chemisorption for H_2S removal.

Keywords : Activated carbon; Adsorption; H_2S removal; Surface oxidation

* ผู้ช่วยศาสตราจารย์, หมวดวิชาวิทยาศาสตร์ประยุกต์ สำนักวิชาการศึกษาทั่วไป มหาวิทยาลัยศรีปทุม

1. Introduction

H_2S is a colorless, highly flammable gas, which in low concentrations has an offensive odor similar to that of rotten eggs. It is a toxic gas that is extremely poisonous even in very small quantities. H_2S is a by-product of oil and gas production operations. It is contained within gas or crude oil underground. Alternatively, H_2S can be produced by microbial decay of sulfur compounds and microbial reduction of sulfate, from geothermal steam, from wood pulping, and from a number of miscellaneous natural sources (Manahan,1993). In addition, H_2S is also released during the decaying of organic materials such as in sewage treatment plants. It has many uses in various industries; for example, in the preparation of metallic sulfides, phosphorus, and oil additives (Chou, 2000).

Adsorption is a simple and inexpensive for removing process, gases and vapors from the air, for example, by passing them through an adsorption bed packed with some solid adsorbents. Thus, air purification applications can be effective where the pollutants are emitted even at very low concentrations (below 100 ppm) but need to be controlled because of their highly malodorous of toxic nature (Theodore and Buonicore, 1994). Activated carbon is the most commonly used adsorbent in odor control applications. It can be produced from a variety of feedstocks such as wood, coal, coconut, nutshells, and petroleum-based products (Mycock, Mckenna, and Theodore, 1995). Although adsorption by activated carbon can be effectively used for air purification but this can not solve the problem fully. In general, any organic compounds having molecular weight greater than 45 is likely to be a good adsorbate on activated carbon (Noll, Gounaris, and Hou, 1992). But the efficiency of activated carbon is poor for low molecular weight gas, in particular H_2S (Spengler, Samet, and McCathy, 2000). These problems have motivated and created interest to study the use of adsorption by increasing the adsorptive efficiency of activated carbon for H_2S elimination from wastewater treatment plants. This is because large quantities of wastewater resulting from chemical and refinery operations must be treated. These effluents are also a source for malodorous elements. H_2S can produce objectionable odor through open tanks, channels, and leaks in sewer systems (Cheremisinoff, 1993).

Efficiency of adsorption can be enhanced by increasing the functional groups such as C-O and / or C=O on the surface of activated carbon, resulting in more active polar adsorption sites. One of the process for increasing the functional groups is by oxidation. Hot air, oxygen gas, potassium hydroxide (KOH), phosphoric acid (H_3PO_4) or nitric acid (HNO_3) may be used as oxidizing agents. HNO_3 is a strong oxidizing agent and is popularly used for increasing the functional groups on activated carbon surface. However this is a complicated procedure,

although used for a long time, it has a high operative cost and requires too much electrical energy (Cal, Strickler, and Lizzio, 2000). Alternatively, an ozone (O_3) oxidation process may be a good choice because it is a stronger oxidizing agent than HNO_3 and thus can be useful in increasing functional groups on surface of activated carbon. In this study attempt was made to improve the adsorption of H_2S by introducing acid surface functional groups on the activated carbon using O_3 and HNO_3 as oxidants and also by the addition of zinc via an ion-exchange (IE) process to further enhance the capture efficiency for H_2S.

2. Method

2.1. Activated carbon

All samples of activated carbon (code No.CGC-11A) in this study were supplied by C. Gigantic Carbon Co.Ltd., in the Province of Nakhon Ratchasima, Thailand. The CGC-11A is a granulated activate carbon (commercial grade) made from coconut shell and has a particle size of 8 x 16 mesh (1800-3600 μm).

2.2 Surface Modification Methods

2.2.1 HNO_3 Oxidation

The concentrations of HNO_3 solution used in this study were 2.0, 4.0, 6.0, 8.0, and 10.0 M with 70% HNO_3 being used as a starting concentrated solution. The original activated carbon sample was put into the HNO_3 solution and the mixture was continuously stirred and heated for 2 hours at 90-105°C in a reflux column. A reflux column was used to prevent excessive HNO_3 loss. After that, the sample was washed thoroughly with distilled water and dried in a hot air oven at 103°C for 12 hours.

2.2.2 O_3 Oxidation

In gas phase oxidation, the original activated carbon weighing about 3.7 g was packed into a fluidized-bed column. The column was constructed from stainless steel pipe (type 304) of 1.2 cm inside diameter and 50 cm in height with a porous hastalloy gas distributor plate at 15 cm above the bottom of the column. The fluidized-bed unit was heated in a tube furnace and installed ozone gas from an ozone-oxygen generator was passed through the column. The ozone generator model, OZ-7501 type corona discharge air cool with ozone capacity 1 g/h and maximum air flow rate of 6 L/min was used for this experiments. Ozone concentration of 1-3% by weight in air can be produced. The experiments were performed in gas phase at variable temperatures between 90 and 250°C, the oxidation period from 30 to 90 minutes and air (O_2) flow rate was kept constant at 5.5 L/min corresponding to gas superficial velocity of 0.79 m/s. The minimum fluidization velocity was estimated to be 0.79 m/s.

In liquid phase oxidation, about 20 g of the original activated carbon sample was mixed with 0.6 L distilled water and loaded in to a reflux column and continuously stirred at 90°C. Then the ozone gas from ozone generator with flow

rate of 1.5 L/min was passed through the solution in the reflux column for different durations of 60, 120 and 180 minutes and the filtered carbon samples were dried in the hot air oven at 103°C for 12 hours.

2.2.3 Metal addition by Ion Exchange (IE)

About 10-20 g of each of the original, HNO_3 oxidation, and O_3 oxidation samples was mixed with zinc acetate [$Zn(C_2H_3O_2)_2$] solution. Zinc ions from zinc acetate solution can attach to the carbon surface by an aqueous ion exchange process. The concentrations of the solution were varied 0.05, 0.10, 0.20, 0.30 and 0.40 M. The mixture solution was continuously stirred for various times of 30, 60, 90, and 120 minutes at room temperature. After completion, the sample was filtered and washed with deionized H_2O and dried in the hot air oven at 103°C for 12 hours.

2.3 Characterization Techniques

2.3.1 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The surface functional groups were identified from transmission infrared spectra obtained from a Fourier transform infrared spectroscopy (Perkin Elmer, model spectrum GX). The analysis was as follows, potassium bromide (KBr) pellet was first prepared by mixing about 1.0 mg of powder activated carbon with about 300 mg of KBr(Merck; for spectroscopy) in an agate mortar. The mixture was compressed under a very high pressure in a special die at 15,000 pounds per square inch to form a small disk about 1 cm in diameter and 1-2 mm thick. The disk is transparent to IR radiation and may be analyzed directly. The FT-IR spectra of the samples were recorded between 4000 and 800 cm^{-1} with 40 scans obtained at 4 cm^{-1} resolution.

2.3.2 Atomic Absorption Spectroscopy (AAs) Analysis

Metal content of zinc impregnated activated carbon samples by IE method was determined using an atomic absorption spectrophotometer (Varian model spectrAA-250 plus). Carbon-based samples were dissolved in hydrochloric acid aqua regia before the analysis. An aqua regia is a mixture of one part by volume of concentrated nitric acid and three parts of concentrated hydrochloric acid. The zinc atoms from atomizer are absorbed at wave length 213.9 nm. Quantitative analysis with atomic absorption spectroscopy technique is based on the determination of the amount of zinc radiation absorbed by the samples.

2.3.3 BET Surface Area and Micropores Analysis

Specific surface area and pore volume of the activated carbon samples were estimated from nitrogen (N_2) adsorption isotherms at 77 K using automatic surface analyzer instrument (Micromeritrics, model : ASAP2010). BET (Brunauer-Emmett-Teller) theory and DR (Dubinin-Radushkevich) equation were used for the determination of surface area and micropore volume, respectively. The total pore volume was

computed from the amount of N_2 gas adsorbed at a relative pressure of 0.98.

2.4 Adsorption tests

The adsorption tests for H_2S removal were performed in a fixed-bed adsorber made of a stainless steel column of 1.2 cm inside diameter. About 3 g of activated carbons (untreated or treated samples) were loaded into the adsorber to a height of approximately 5.5 cm. A mixture of 1.01wt% H_2S in balance N_2 was allowed to flow in to the adsorption column at a constant flow rate of 150 cm^3/min. The exit concentration of H_2S was continuously monitored by the electro-chemical sensor (Q-RAE PLUS, model PGM 2000) every 5 seconds. The breakthrough curves so obtained can be used to estimate the breakthrough time, and the amount of H_2S removed. The effect of temperature on the adsorption performance was studied at temperatures 10, 30, and 45°C.

3. Results and Discussion

3.1 FT-IR spectra of the O_3 oxidized samples in gas phase

Because of the highly reactive nature of O_3 and of the complex surface chemistry of the activated carbon, a number of competitive reactions may occur when O_3 was brought into contact with the activated carbon samples. The reactions may involve free radicals of high oxidation potential that could initiate chain reactions, which in turn further provoke the decomposition of more O_3 on the activated carbon surface (Gomez-Serrano, et al., 2002). As a result, it is not an easy task to predict a simple mechanism for the ozonation of the activated carbon. Molecular ozone is able to act as a 1,3-dipole, an electrophile, or a nucleophile (Gomez-Serrano, et al., 2002). The electrophilic ozonolysis of carbon-carbon double bonds in olefinic structures is expected to occur in a process involving three steps: (1) 1,3-dipolar addition of O_3 to the double bond to give an unstable primary ozonide; (2) decomposition of ozonide by a 1,3-dipolar reversion to yield a carbonyl compound and a carbonyl oxide; (3) the carbonyl oxide may give a normal ozonide, dimerizes to aldehyde or ketone diperoxides, or polymerizes to give polymeric peroxides or ozonide (Gomez-Serrano, et al., 2002). In fact, peroxides, ozonides, and carbonyl structures may be found in the ozonation products of activated carbon. Figure 1 shows typical FT-IR spectra for the samples oxidized with O_3 in fluidized-bed at various treatment times and temperatures. All spectra of these samples display weak bands at 2907, 2840, and 2320 cm^{-1} which are connected with ν_{as}(C-H), ν_S(C-H) vibrations (s=symmetric, as=asymmetric) and assigned to carbon-oxygen groups, respectively. The spectra for C and D samples show the intensity of the bands at 1108, 1556, 1618, and 1702 cm^{-1}. The bands at 1108, 1156, and 1618 cm^{-1} are due to ν(C-O) vibrations in aliphatic ether, ν(C=C) vibrations in haloalkene, and ν(C=C) vibrations in alkene, respectively. The band at

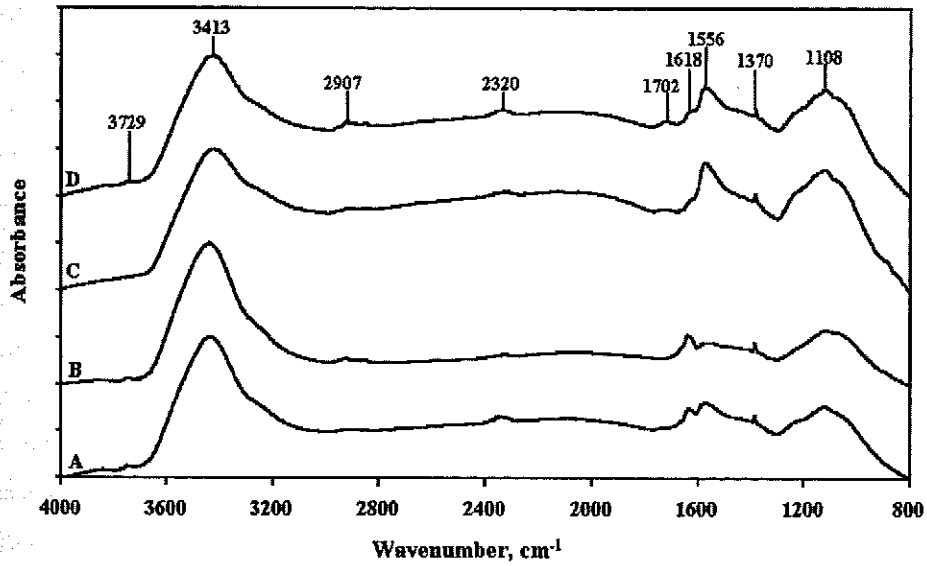

Fig.1 FT-IR spectra of O_3 oxidized samples in fluidized-bed. An air (O_2) flow rate 5.5 L/min at various temperatures and times of: A= 180°C, 30 min, B= 240°C, 30 min, C= 180°C, 90 min, D=190°C, 60 min.

1702 cm^{-1} was attributed to ν(C=O) vibrations in ketone, which is not present in the spectra of A and B samples. The same time treatment for 30 minutes of A and B samples shows similar spectra and the band intensities are less than those of C and D samples.

3.2 FT-IR spectra of the O_3 oxidized samples in liquid phase

The FT-IR spectroscopy results for the ozone oxidized samples in a reflux column (hot water, 90°C) compared with the original sample are shown in Figure 2. The broad band at 1111 cm^{-1} with a shoulder at 1030 cm^{-1} is due to hydroxyl group in primary aliphatic alcohol is showing in the spectra of B, C, and D. The bands centered near 2300 cm^{-1} are assigned to carbon-oxygen groups due to ketone (Jae-Woon, et al., 2001) or CO_2 contamination (Chen, et al., 2003), which is not present in the spectrum of A. Two shoulders at 3842 and 3725 cm^{-1} in spectra of samples B, C and D are due to ν(O-H) vibrations of hydrogen bonding.

3.3 FT-IR spectra of HNO_3 oxidized samples

Surface oxygen complexes are formed on activated carbons when they are oxidized with HNO_3 in a reflux column. Fixation of the acidic groups on the surface of activated carbons makes it more hydrophilic and it also effects the surface area and pore texture of the activated carbons (Pradhan and Sandle, 1999). The change in the surface chemistry of activated carbon due to the

formation of acidic oxygen complexes will effect the behavior of the samples when they are used as adsorbents. Comparison of FT-IR spectra for the original sample with HNO_3 oxidized samples is shown in Figure 3. The FT-IR spectrum of the original sample presents the intensity of the bands at 1116, 1572, 1616, and 3417 cm^{-1} due to ν(C-O) vibrations in aliphatic ether, ν(C=C) vibrations in haloalkene, ν(C=C) vibrations in alkene, and hydroxyl groups in hydrogen bonding, respectively. The HNO_3 oxidized samples as well as the original sample spectra have a broad absorption band extended between 1000 and 1300 cm^{-1}. This has been assigned to ν(C-O), and δ(O-H) vibrations of alcoholic, phenolic, and carboxylic groups. This peak has a shoulder at 1126 cm^{-1}, which is expected to be due to carboxylic-OH group. The band at 1705 cm^{-1} can be assigned to the ν(C=O) vibrations from ketones, aldehydes, or carboxylic groups. For the activated carbon oxidized with HNO_3 there is a large increase in the intensity of the band at 1705 cm^{-1}, which is not present in the original sample. In this study, the intensity of the band at 1705 cm^{-1} depended on the concentrations of HNO_3 used for treatment of the activated carbon samples.

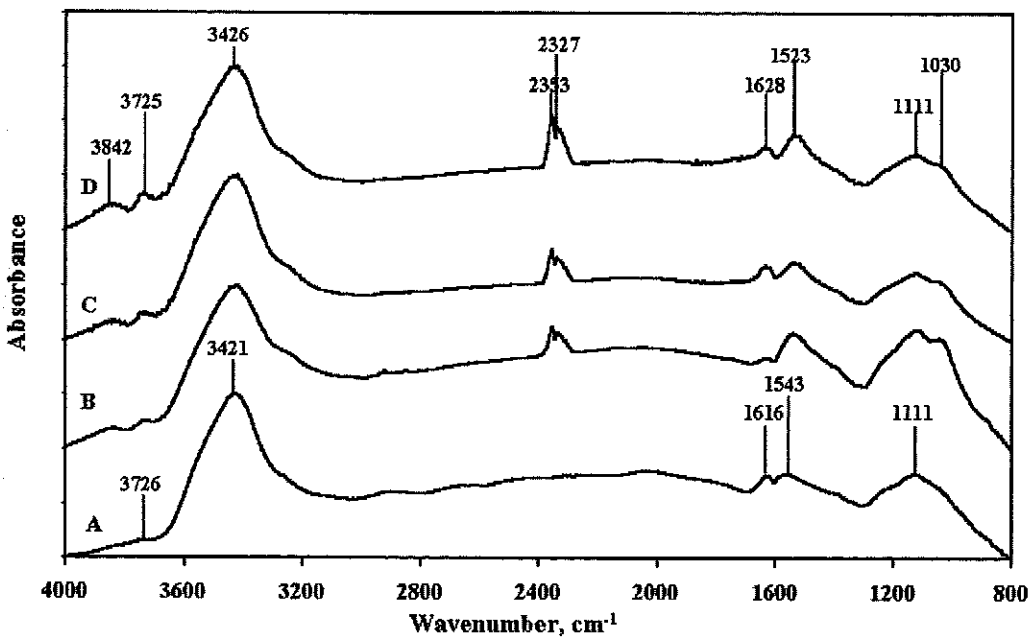

Fig.2 Comparison of FT-IR spectra for the original sample A with ozone oxidized samples in reflux column (ozone gas flow rate 1.5 L/min at various times of: B=60 min, C=120 min, D=180 min).

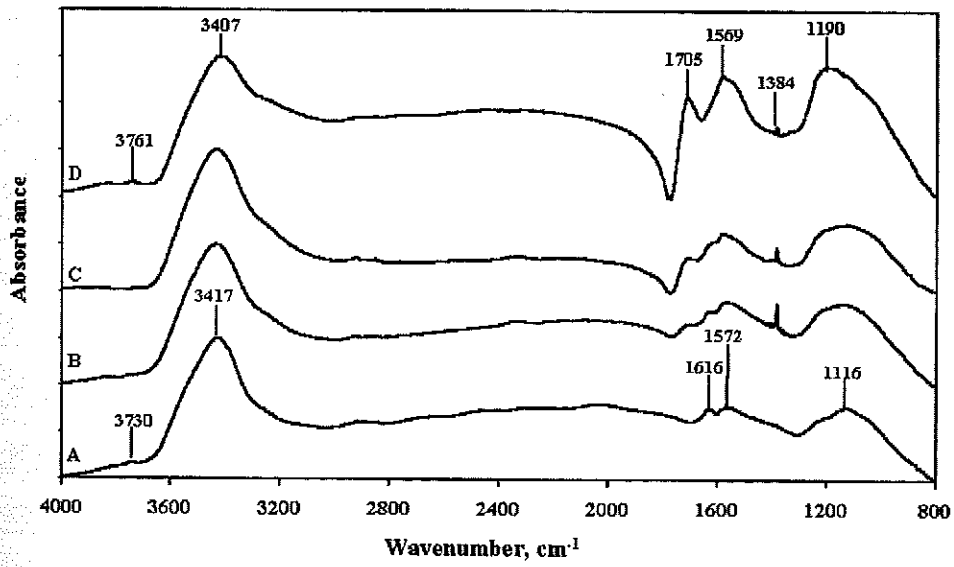

Fig. 3 Comparison of FT-IR spectra for the original sample A with HNO_3 oxidized samples at 105°C for 120 min (HNO_3 concentration: B=2.0 M, C=6.0 M, D=10.0 M)

3.4 Atomic Absorption Spectrometry Analysis

Metal content of zinc impregnated carbon-base sorbent by ion exchange method was determined using atomic absorption spectrometry. Zinc content of the original samples by ion exchange method was found to be between 22.07 and 28.13 mg-Zn^{2+}/g-sample for the range of 0.05-0.4 M zinc acetate concentration impregnated at room temperature for 90 min. The increase in zinc content of samples depended on the contact time in an ion exchange process. In this study, when the ion exchange process was fixed at room temperature and zinc acetate solution of 0.2 M, the highest zinc content of 32.81 mg-Zn^{2+}/g-sample was obtained at 120 min and the lowest is 16.17 mg-Zn^{2+}/g-sample at 30 min contact time.

The amount of zinc ion added to the oxidized samples (O_3 and HNO_3 oxidation) is given in Table 1. An oxidized sample was heat treated to a higher temperature for O_3 oxidation in fluidized-bed at 210°C for 90 min, and the amount of zinc ion is found to be 36.04 mg-Zn^{2+}/g-sample. In the case of O_3 oxidation in a reflux column at 90°C, the amount of zinc ion on surface area of these samples decreased when the contact time used for O_3 oxidation was increased. Trend of the increasing zinc ion uptake on surface area of the impregnated samples depended on the HNO_3 concentrations which were used for oxidation process. In this case, sample oxidized with 10.0 M HNO_3, the zinc content is maximum while with 2.0M HNO_3, it is minimum.

Table 1. Amount of zinc ion added to activated carbon sample, Zn^{2+} added to all samples by ion-exchange (0.2 M zinc acetate).

Sample description			Sample wt.(g)	Zinc conc. (ppm)	mg Zn^{2+}/g-sample
Oxidation methods	Maximum temp. (°C)	Time (min)			
O_3 oxidation in fluidized-bed	150	60	0.1177	1.6	13.59
	180	30	0.1048	1.8	17.18
	190	60	0.1120	2.0	17.86
	210	90	0.1304	4.7	36.04
O_3 oxidation in hot water(reflux)	90	60	0.1300	4.8	36.92
	90	120	0.1308	3.4	25.99
	90	180	0.1299	3.2	24.63
2.0M HNO_3 oxidation (reflux)	90	120	0.1084	2.2	20.30
6.0M HNO_3 oxidation (reflux)	105	120	0.1234	3.9	31.60
10.0M HNO_3 oxidation (reflux)	110	120	0.1175	6.2	52.77

3.5 Nitrogen isotherms

Nitrogen adsorption isotherm is a standard tool for the characterization of porous materials especially porous carbonaceous adsorbents. The adsorption isotherm can yield valuable information concerning surface area and pore structure of adsorbent, heat of adsorption and so on (Pradhan and Sandle, 1999). However, the specific surface areas of activated carbon are decreased by the chemical oxidation and metal addition. In Figure 4 the nitrogen adsorption isotherms on the untreated activated carbon, 6.0 M, HNO_3, 6.0 M HNO_3 +Zn^{2+}, and 10.0 M HNO_3 + Zn^{2+} are compared in order to show the differences in their adsorption capacity and isotherm type. The treated activated carbons cause the downward shift of the isotherms. In the case of sample oxidized with 10.0 M HNO_3 and Zn^{2+} addition, the shift is maximum. All the isotherms can be classified as the type I isotherm which is typical of adsorption in microporous solids (Do, 1998). The lowering of N_2 adsorption of modified activated

carbons suggests that some of the pores may be blocked by oxide functional groups introduced during the chemical treatment.

3.6 Surface area and porosity analysis

Figure 5 shows typical SEM image of the original activated carbon sample structure. Table 2 shows the results of surface area and pore volume of the original and treated activated carbons. The change in surface area with different treatments increases in the following order, 10.0 M HNO_3+Zn^{2+} > 6.0 M HNO_3+Zn^{2+} > 6.0 M HNO_3. The BET surface area considerably decreased due to the blocking of the narrow pores by the surface complexes introduced during HNO_3 treatment. Therefore, oxygen surface groups are expected to locate at the edges of the basal planes which are relatively weak sites of carbon structure and oxidation progresses slowly into the basal planes (Jae-Woon, et al., 2001). The micropore volume decreases with oxidation and zinc ion addition in activated carbon, in the case of 10.0 M HNO_3 the decrease was maximum. Similarly this is a result of the fixation of surface oxygen complexes essentially at the entrance of the pores, which increases their constriction or in other word not all the micropores are accessible to N_2 molecule, (Pradhan and sandle, 1999). The decrease of surface area was mainly ascribed to the decrease of the micropore volume.

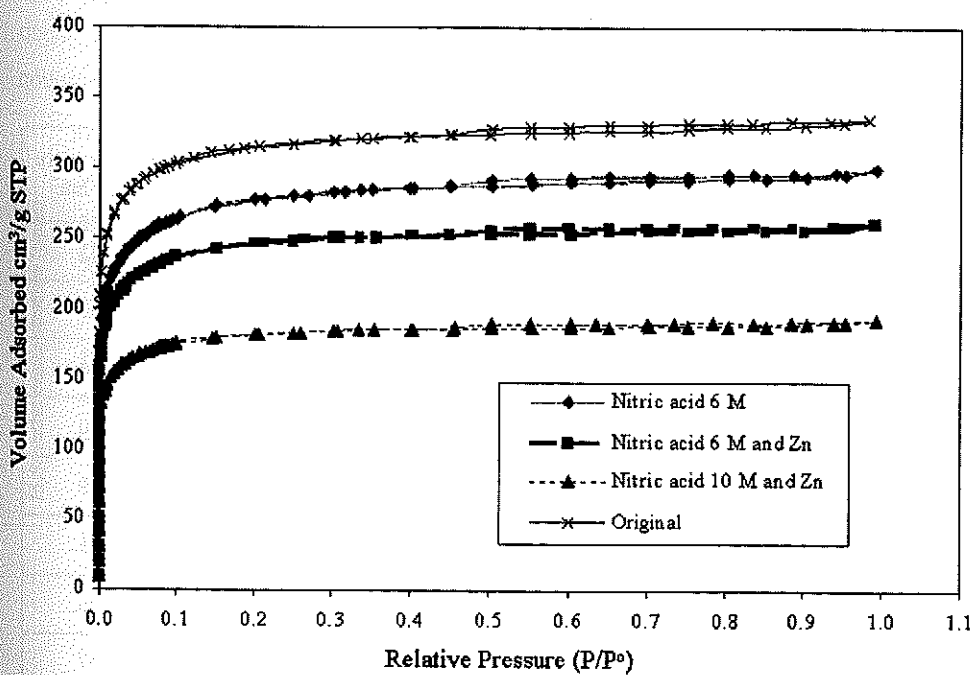

Fig. 4 Adsorption isotherms of N_2 on untreated and treated activated carbons at 77 K

3.7 Breakthrough Curve Experiments by Electrochemical Sensor

The term breakthrough used throughout this paper is referred as a condition at with a certain concentration of H_2S has not been removed by the carbon bed or H_2S has broken through (Cal, et al., 2000). Breakthrough in all H_2S adsorption experiments is defined as OSHA:ceiling 20 ppm H_2S outlet concentrations, which are the exposure limits (TWA value). Breakthrough time is the time that the outlet gas H_2S concentrations reaches 20 ppm. Time-Weighted Average(TWA) is the average concentration of contaminants over a specified time period. Ceiling limit is the concentration which should not be exceeded at any time (Chou, 2000).

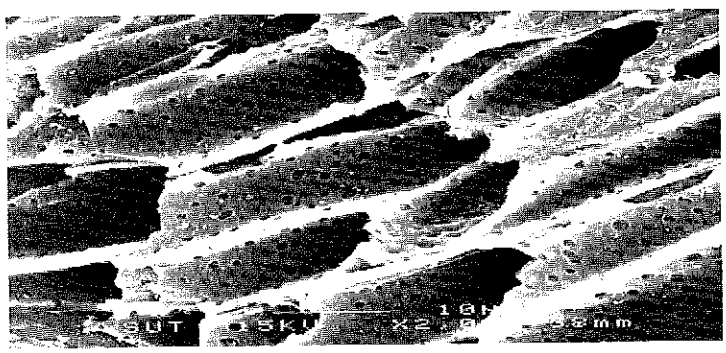

Fig. 5 Typical SEM image of internal activated carbon structure obtained from the original sample

Table 2 Specific surface areas and porosities in activated carbon samples by N_2 adsorption

Sample	Surface area analysis; m^2/g			Pore volume; cm^3/g		Average pore size; nm
	Total	Micropore	External	Micropore	Total	
Original	1119	879	240	0.38	0.52	1.85
Original+ Zn	967	767	200	0.37	0.49	2.02
6M HNO_3	909	640	269	0.31	0.46	2.04
6M HNO_3+Zn	808	593	215	0.28	0.40	1.20
10M HNO_3+Zn	597	454	143	0.22	0.30	2.00
O_3 (fluidized-bed 210°C)+ Zn	967	767	200	0.37	0.49	2.01
O_3(reflux 60 min) + Zn	959	791	168	038	0.47	1.98
O_3 (reflux 120 min) + Zn	962	783	179	0.37	0.47	1.97
O_3 (reflux 180 min) + Zn	957	766	191	0.36	0.47	1.99

3.7.1 Adsorption of untreated activated carbons

Figure 6 shows H_2S breakthrough times for the original samples at different temperatures. Three experiments were performed with the temperature varying between 10 and 45°C using 1.01% H_2S plus balance N_2. All breakthrough times, reaching 20 ppm at 10, 30, and 45°C, were 1095, 645, and 700 seconds, respectively. In the case of the original sample, adsorption of gas molecules on activated carbon is dominated by the van der Waals forces which is physical in nature. In addition ,the small pore sizes and large surface area of activated carbon play the major role in gas adsorption (Yang, 2003). The maximum breakthrough time occurred at 10°C, because the physical adsorption rate increases with decreasing temperature.

3.7.2 Adsorption of treated activated carbons

Breakthrough times at 20 ppm for H_2S adsorption experiments performed using the same fixed-bed for 6.0 M HNO_3 oxidation and Zn addition are shown in Figure 7. HNO_3 oxidation and Zn addition treated carbon exhibited longer breakthrough times than the untreated carbon samples (see Fig. 6 for comparison). The best performing sample had the longest breakthrough time for H_2S removal at 45°C which can be ascribed to the role of chemisorption. The chemisorption involves chemical bonding, and chemisorbed molecules are fixed at specific sites (Noll, et al., 1992). A gas molecule must be capable of forming a chemical bond with the adsorbent surface for the chemisorption to occur and chemisorption forms only a monolayer of adsorbate

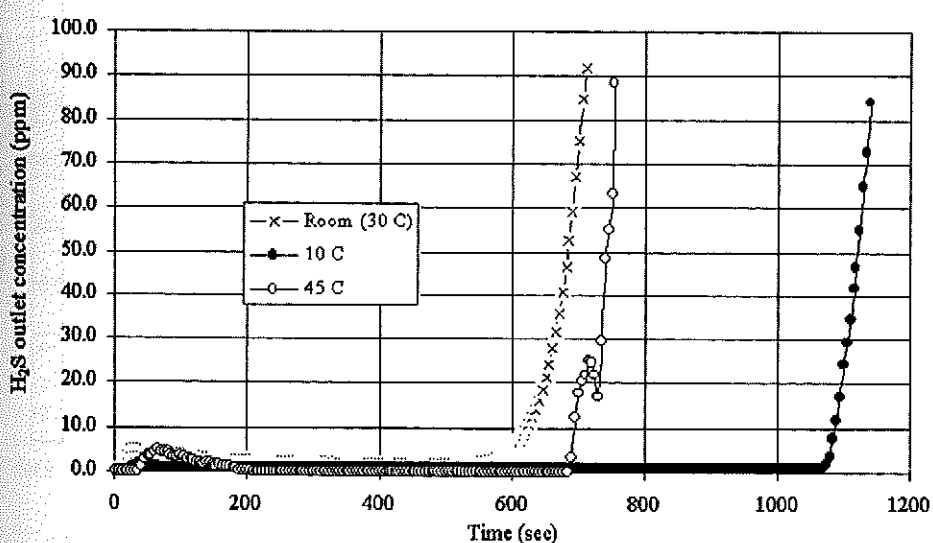

Fig. 6 Comparison of H_2S breakthrough times for the original activated carbon samples at various temperatures. Gas composition: 1.01% H_2S, balance N_2. P=1.0 bar.

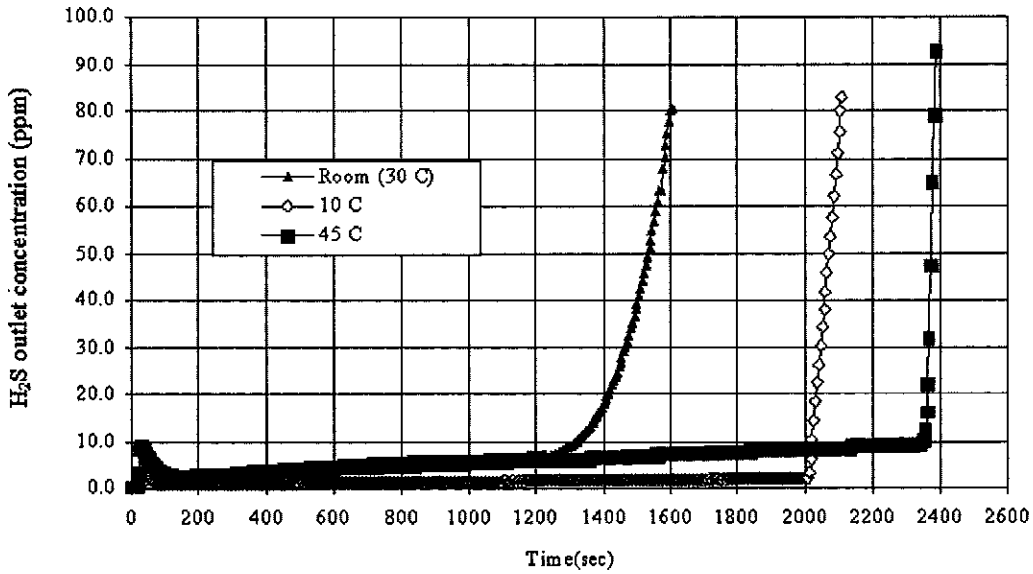

Fig. 7 Comparison of H_2S breakthrough times for 6.0 M HNO_3 oxidized and Zn impregnated samples at various temperatures. Gas composition: 1.01% H_2S, balance N_2. P=1.0 bar.

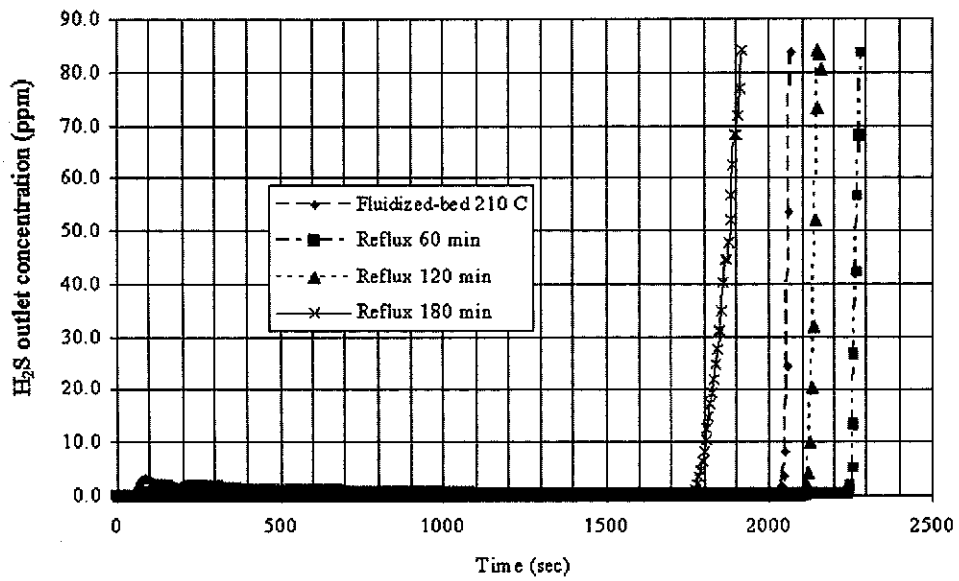

Fig. 8 Comparison of H_2S breakthrough times for O_3 oxidized and Zn impregnated samples at 10°C, P=1.0 bar, with different conditions. Gas composition: 1.01% H_2S, balance N_2.

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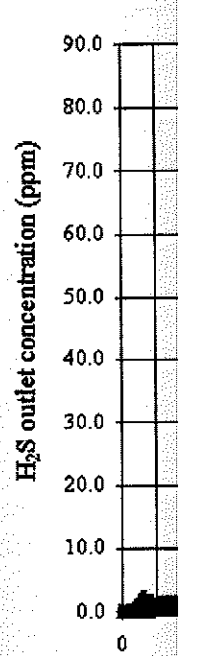

Fig. 9 Comp
30°C,

molecules on the surface (Mycock, et al.,1995). The chemisorption rate increases with increasing temperature; however, heat of adsorption is not usually a definite criterion. From these experiments, it can be concluded that the structure of the activated carbon samples is probably the most important factor affecting the primary adsorption process. However, the surface chemistry is another important factor. Comparison of H_2S breakthrough times from the O_3 oxidized and Zn impregnated samples at various temperatures 10, 30 and 45°C are shown in Figures 8, 9, and 10 respectively. Most of the breakthrough curves at 10°C (see Fig. 8) give longer breakthrough times than the breakthrough curves at 45°C (see Fig.10), indicating dominant role of physical adsorption for H_2S removal. Alternatively, the results at 45°C are better than the results at 30°C (see Fig. 9), largely due to the effect of chemical adsorption on H_2S removal.

The amounts of H_2S removal in mg-H_2S/g-sample from some samples in this study are summarized in Table 3. The H_2S ceiling limit from the Occupational Safety and Health Administration (OSHA) for use in promulgating legal standards is 20 ppm. Thus, the concentration

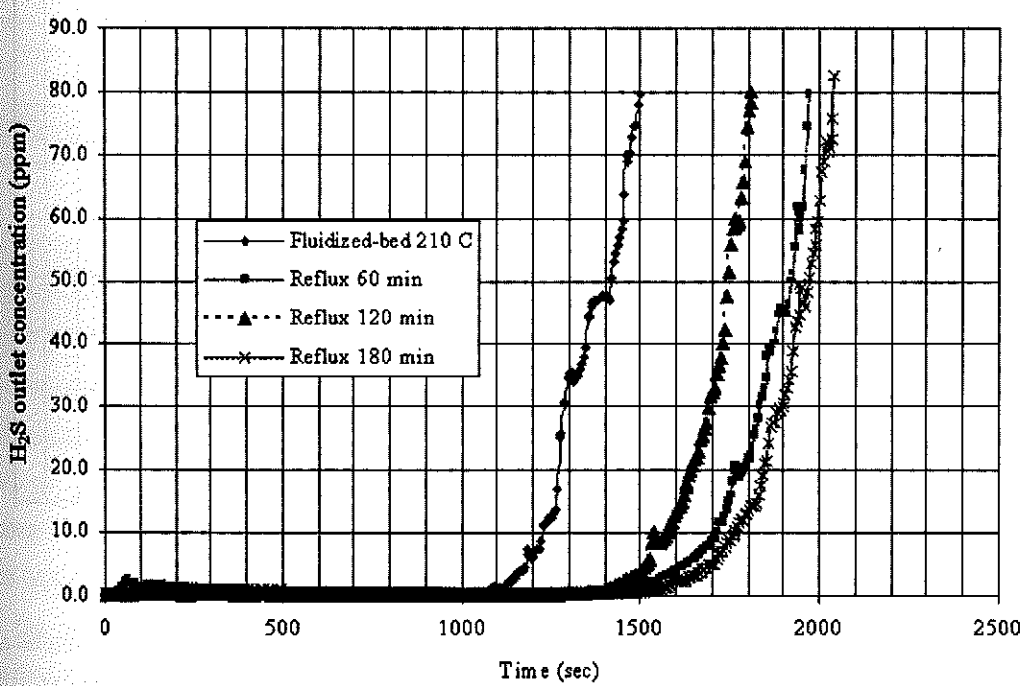

Fig. 9 Comparison of H_2S breakthrough times for O_3 oxidized and Zn impregnated samples at 30°C, P=1.0 bar, with different conditions. Gas composition: 1.01% H_2S, balance N_2.

of H_2S (20 ppm) should not be exceeded at any time. Zn impregnation of the original samples removed 17.09 and 16.39 mg-H_2S/g-sample at 10 and 45°C, respectively. The increasing percentage for removal H_2S was approximately 118% over that of the original sample at 45°C. The carbon sample treated with 6.0 M HNO_3 and Zn impregnation gave the highest adsorption capacity for H_2S, giving increased adsorption efficiency of 230% over that of the untreated sample at 45°C. At the lowest temperature(10°C) the O_3 oxidized (reflux, 60 min) sample impregnated with Zn adsorbed 24.19 mg-H_2S/g-sample giving the highest removal efficiency. The maximum increase of 180% adsorption efficiency at 30°C over that of the original sample was observed with the O_3 oxidized (reflux,180min) sample impregnated with Zn. There was a tendency that the chemical adsorption of H_2S increased with the amount of Zn impregnated on the surface sample at temperatures of adsorption higher than 45°C, indicating the significant role of chemisorption for H_2S removal under this condition.

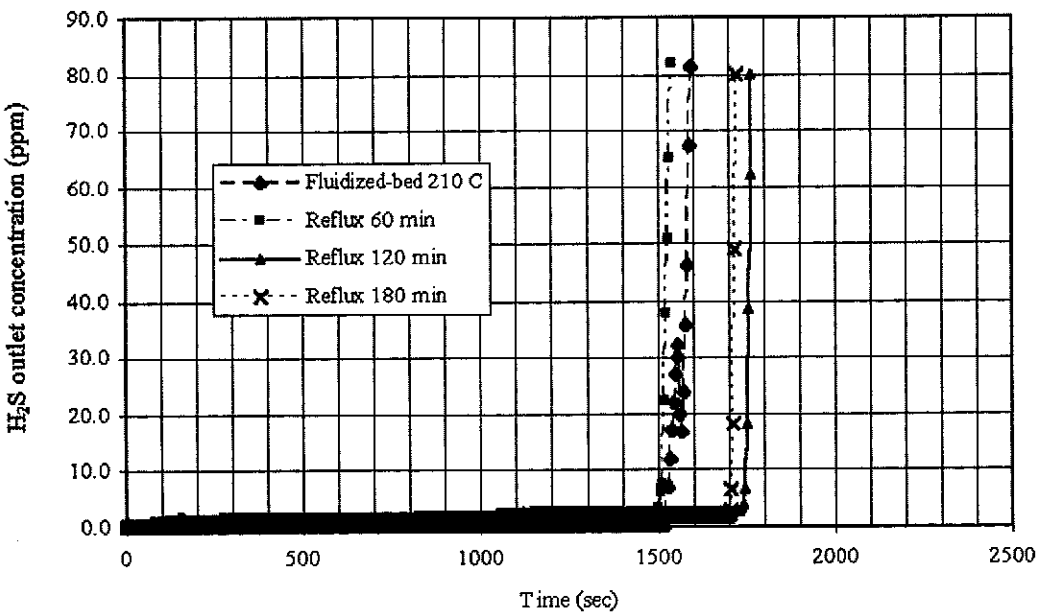

Fig.10 Comparison of H_2S breakthrough times for O_3 oxidized and Zn impregnated samples at 45°C, P=1.0 bar, with different conditions. Gas composition: 1.01% H_2S, balance N_2.

Table 3 Summary of H_2S removal experiments

Sample description	OSHA: ceiling=20 ppm (mg-H_2S/g-sample)			Percentage increase for H_2S removal		
	Adsorption (10°)	Adsorption (30°)	Adsorption (45°)	Temp. 10°C	Temp. 30°C	Temp. 45°C
Original	11.70	6.87	7.49	-	-	-
Original+ Zn	17.09	-	16.39	46.1	-	118.8
6.0 M HNO_3 + Zn	21.65	15.02	24.72	85.0	118.6	230.0
O_3 (fluidized-bed 210°C) +Zn	21.93	13.63	16.52	87.4	98.4	120.6
O_3(reflux 60 min) + Zn	24.19	18.83	16.28	106.8	174.2	117.3
O_3 (reflux 120 min) + Zn	22.77	17.59	18.66	94.6	156.0	149.2
O_3 (reflux 180 min) +Zn	19.58	19.24	18.31	67.4	180.0	144.4

4. Conclusions

FT-IR spectroscopy is a useful tool to determine the chemical structure of the original activated carbon and the oxidized samples. The formation of oxygen components such as ester, alcohol, ether structures, ketone, and carboxylic acid groups are found. The ozonation of activated carbons is a very effective method to form a variety of oxygen complexes, the concentration and type of which may be markedly influenced by the times and temperatures of ozonation. On the basis of the results, it has been suggested that 210°C, 90 min in fluidized-bed and 90°C,180 min in a reflux column are the most suitable ozonation conditions of the original activated carbon. In the case of the original activated carbon modified with HNO_3, this oxidation treatment gives rise to a large increase in the amount of total acidity. The intensity of the acidic groups depended on the concentrations of HNO_3 which are used for the treatment.

The amount of Zn metal obtained from the Zn impregnated samples by IE method depended on the concentrations and type of oxidizing reagents. The maximum quantity of Zn metal obtained from the Zn impregnated samples after oxidized with the O_3 in fluidized-bed reactor, O_3 in a reflux column, and HNO_3 in a reflux column are 36.04, 36.92, and 52.77 mg-Zn/g-sample, respectively. They were also found that the lower

surface area carbon samples contain a higher density of carbon surface functional groups such as C-O and C=O, resulting in more active polar ion-exchange sites.

The N_2 adsorption isotherms of all samples gave the type I isotherms (monolayer coverage) characterized by a plateau that is nearly horizontal to the P/P^o axis, typical of adsorption in micro-porous solids. The BET surface area is considerably decreased due to the blocking of the narrow pores by the surface complexes introduced by oxidizing reagents and/or Zn impregnated treatments. The decrease of surface area was mainly ascribed to the decrease of the micropore volume. The micro-porous structure of the activated carbon sample is the most important factor that affects the adsorption properties.

A synthetic gas mixture of 1.01wt % H_2S plus balance N_2 was used for the fixed-bed adsorption experiments. The outlet concentration of H_2S from the fixed-bed adsorber was followed as a function of time by electrochemical sensor. Adsorption capacity (mg H_2S adsorbed/g adsorbent) up to the breakthrough time was used to assess the efficiency of H_2S removal. Zn-impregnated samples gave higher adsorption capacity than the single-step oxidized samples and an untreated samples at temperatures of 10, 30 and 45°C.

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