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Adsorptive Removal of Vapors of Toxic Sulfur Compounds using Activated Carbons

Meenakshi Goyal and Rashmi Dhawan

***Abstract*—**Adsorption of CS_2 vapors has been studied on different types of activated carbons obtained from different source raw materials. The activated carbons have different surface areas and are associated with varying amounts of the carbon-oxygen surface groups. The adsorption of CS_2 vapors is not directly related to surface area, but is considerably influenced by the presence of carbon-oxygen surface groups. The adsorption decreases on increasing the amount of carbon-oxygen surface groups on oxidation and increases when these surface groups are eliminated on degassing. The adsorption is maximum in case of the 950°-degassed carbon sample which is almost completely free of any associated oxygen. The kinetic data as analysed by Empirical diffusion model and Linear driving force mass transfer model indicate that the adsorption does not involve Fickian diffusion but may be considered as a pseudo first order mass transfer process. The activation energy of adsorption and isosteric enthalpies of adsorption indicate that the adsorption does not involve interaction between CS_2 and carbon-oxygen surface groups, but hydrophobic interactions between CS_2 and C-C atoms in the carbon lattice.

***Keywords*—**Adsorption, surface groups, adsorption kinetics, isosteric enthalpy of adsorption.

I. Introduction

VAPORS of sulfur containing organic compounds such as carbon disulfide (CS_2) and dimethyl sulfide (DMS) are highly obnoxious and toxic. While CS_2 is derived from several industrial processes and is also produced in nature by different anaerobic degradation processes, DMS is produced during cooking of seafood and is a metabolic product of many biosystems. DMS is also produced abundantly by marine algae. Oceanic DMS emissions account for 15% of the total global sulfur emissions. Both these compounds cause various respiratory and other body ailments depending upon the short time or the long time exposure to these vapors. It is thus essential to develop suitable adsorbents for their removal from working places of several industrial units and from the inhabited places of the ships over the sea.

Several types of adsorbents such as silica [1-3], alumina [5] zeolites [1-3] and activated carbons [1-4] are available, but more attention has been directed towards activated carbons because of their large surface area, a highly microporous structure and a high degree of chemical reactivity of their surface. A perusal of the literature [1-8] shows that the adsorption of activated carbons for these vapors has largely been attributed to their surface area and micropore structure, little attention being paid to the presence of carbon oxygen groups which are invariably associated with the activated carbon surface. As these surface groups are known to influence the adsorption properties of the activated carbons, the present work has been initiated. In the present paper, the adsorptive removal of CS_2 will be discussed using activated carbons obtained from different source raw materials and having different surface areas and microporous structure and associated with varying amounts of the carbon-oxygen surface groups.

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II. Results And Discussion

A. *Adsorption Isotherms*

The adsorption isotherms of CS_2 vapors on the two samples of granulated activated carbons (GAC-1240 and GAC-R), a sample of activated carbon fiber (ACF–307), a sample of activated carbon cloth (ACC) and a sample of spherical carbon are presented in Fig. 1.

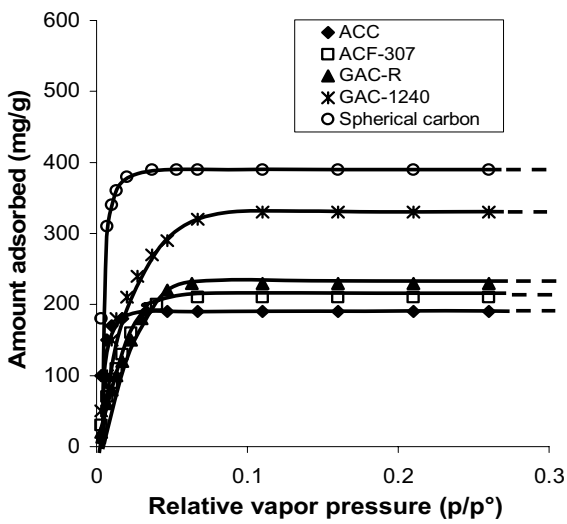

Fig. 1 Adsorption isotherms of carbondisulfide vapors on as-received activated carbons

All activated carbons adsorb appreciable amounts of CS_2 vapor. The maximum amount adsorbed increases with surface area of the carbon, but there is no linear relationship between the amount adsorbed and the surface area. The adsorption data fit the Langmuir adsorption isotherm equation. The linearised forms of Langmuir equation can be represented as

$$\frac{p}{x} = \frac{1}{x_m b} + \frac{p}{x_m}$$

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where x is the amount adsorbed at any pressure p, x_m is the monolayer capacity, and b is a constant related to the energy of adsorption. The linear Langmuir plots are presented in Fig. 2.The monolayer capacity x_m values obtained from these linear plots have been used to calculate the surface area occupied by CS_2 vapors using 0.26 nm^2 as the molecular area for carbondisulfide. These values along with the BET surface area are given in Table I. It is seen that only a fraction of the activated carbon surface varying between 40-70% is occupied by these vapors. This indicates that the adsorption takes place on certain specific sites on the carbon surface. Alternatively some of the micropores on the carbon surface have small entrances which inhibit the entry of larger CS_2 molecules (Molecular diameter = 0.37 nm).

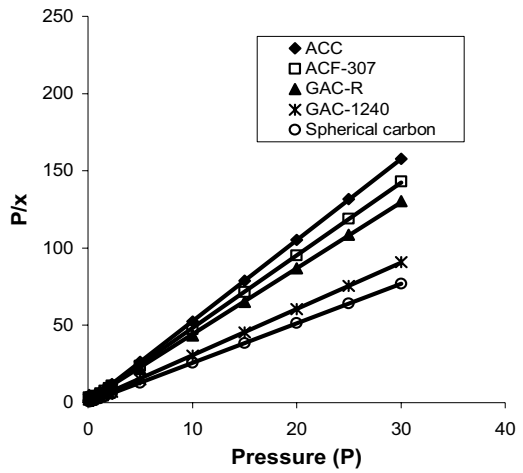

Fig. 2 Linear Langmuir plots for the adsorption of carbondisulfide vapors on as-received activated carbons

B. *Effect of Chemical Structure on Adsorption*

The chemical structure of an activated carbon surface is due to the presence of chemisorbed oxygen which is present in the form of carbon oxygen surface groups [9-11]. These carbon oxygen surface groups are evolved as CO_2, CO and water on degassing in vacuum or in inert atmosphere. The amount of each surface group eliminated depends on the temperature of degassing. The surface groups, which are evolved as CO_2 on degassing in the temperature range 400-750 ^oC are acidic in character [12-15] and have been identified as carboxyls and lactones. The other surface groups are eliminated as CO in the temperature range 500-950 ^oC. These surface groups are non acidic and have been identified as quinones [13, 14]. The acidic surface groups render the carbon surface polar and hydrophilic while the non-acidic surface groups make the carbon surface hydrophobic in character. The amounts of these two types of surface groups depend upon the source raw material and the history of formation of the activated carbon. Furthermore, the amounts of both these surface groups can be enhanced by the oxidation of the carbon surface.

TABLE I
SURFACE AREA OCCUPIED BY CS_2 MOLECULES FOR VARIOUS AS-RECEIVED ACTIVATED CARBONS

Carbon Sample	BET (N_2) Surface area (m^2/g)	Surface area occupied by CS_2 molecules (m^2/g)
ACC	792	383
ACF-307	910	444
GAC-R	1150	478
GAC-1240	1175	665
Spherical Carbon	1200	792

In order to determine the influence of these carbon-oxygen surface groups on the adsorption, two of the carbon samples (ACC and GAC-1240) were oxidized with nitric acid, hydrogen peroxide and ammonium persulphate in the solution phase. The adsorption isotherms on the oxidized carbon samples are presented in Fig. 3 for GAC-1240 and in Fig. 4 for the ACC.

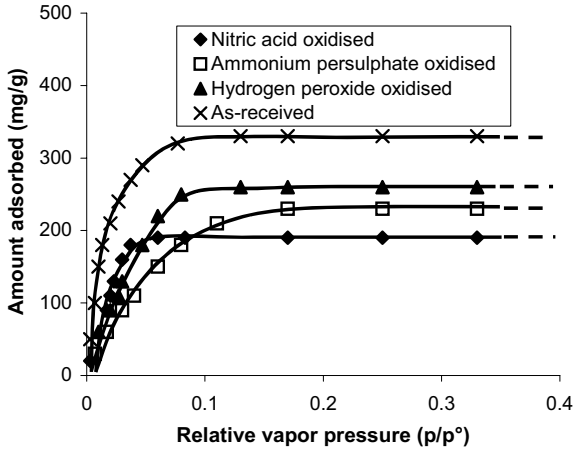

Fig. 3 Adsorption isotherms of carbondisulfide vapors on GAC-1240 sample before and after oxidation

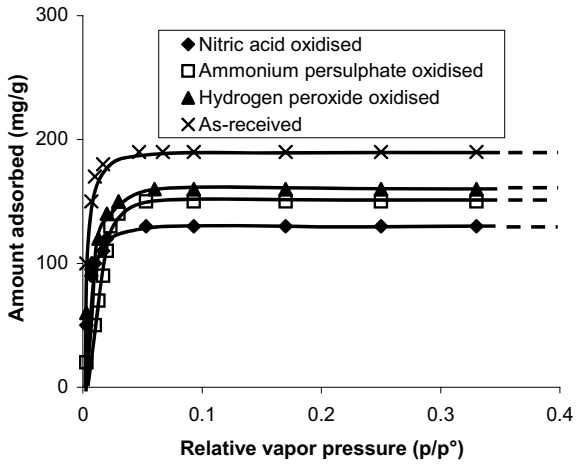

Fig. 4 Adsorption isotherms of carbondisulfide vapors on ACC sample before and after oxidation

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The adsorption isotherms on the as-received carbon samples are reproduced in these figures for an easy comparison. It is seen that each oxidative treatment results in an appreciable decrease in the amount of adsorption, the decrease being maximum in case of the nitric acid oxidized sample. Incidentally, the oxidation with nitric acid is a stronger oxidative treatment and results in the fixation of larger amounts of oxygen and the formation of larger amounts of carbon-oxygen surface groups (cf Table II). The amount of associated oxygen increases from 4.6 % in the case of as-received GAC-1240 to 21.6 % on oxidation with nitric acid and only to between 11-15 % in the case of other oxidations. It appears that the adsorptive removal of CS_2 vapors by activated carbons is influenced considerably by the presence of carbon- oxygen surface groups.

The oxidized carbon samples were then degassed in vacuum at increasing temperatures of 400°, 650° and 950°C. This treatment eliminates varying amounts of the carbon-oxygen surface groups depending upon the temperature of degassing. The adsorption isotherms on the degassed carbon samples are shown in Figs. 5 and 6. It is interesting to note that the adsorption of CS_2 vapors increases gradually as the temperature of degassing is enhanced. The increase is only small when the degassing is carried out at 400 °C. This is due to the fact that at this temperature, only small amount (~15%) of the carbon-oxygen surface groups is eliminated. The adsorption of CS_2 vapors is maximum in case of the 950°-degassed samples which are almost completely free of all carbon oxygen surface groups. This could partly be due to the removal of bulky oxygen surface groups so that the pores are now available for adsorption of CS_2.

TABLE II
SURFACE ACIDITY AND CARBON-OXYGEN SURFACE GROUPS EVOLVED ON DEGASSING DIFFERENT OXIDIZED CARBON SAMPLES AT 950°C

Sample Identification	Surface acidity (mEq. /100 g)	Oxygen evolved (g/100g) as			
		CO_2	CO	H_2O	Total
GAC-1240					
As-received	138	2.35	1.02	1.24	4.61
HNO_3-oxidized	820	13.52	6.82	1.21	21.55
$(NH_4)_2S_2O_8$-oxidized	375	6.21	7.29	1.35	14.85
H_2O_2-oxidized	186	3.12	6.78	1.19	11.09
ACC					
As-received	125	1.92	3.15	1.31	6.38
HNO_3- oxidized	370	6.53	7.52	1.29	15.34
$(NH_4)_2S_2O_8$-oxidized	208	3.29	6.91	1.34	11.54
H_2O_2-oxidized	172	2.82	6.41	1.23	10.46

It appears that the adsorption of CS_2 vapors is suppressed by the presence of carbon oxygen surface groups. The adsorption decreases when the amount of these surface groups is enhanced on oxidation and increases when these surface groups are removed on degassing. A relationship between the maximum amount of CS_2 vapors adsorbed at saturation vapor pressure and the amount of carbon-oxygen groups present on the carbon surface is shown in Fig. 7. It is seen that all the points for a given carbon can be collected along a straight line. Two different straight lines for the two carbons can be attributed to a difference in the microporous structure of the two carbons.

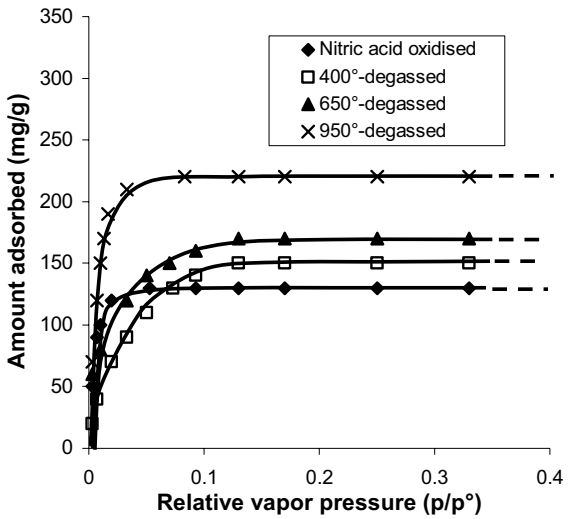

Fig. 5 Adsorption isotherms of carbondisulfide vapors on HNO_3-oxidised ACC sample before and after degassing

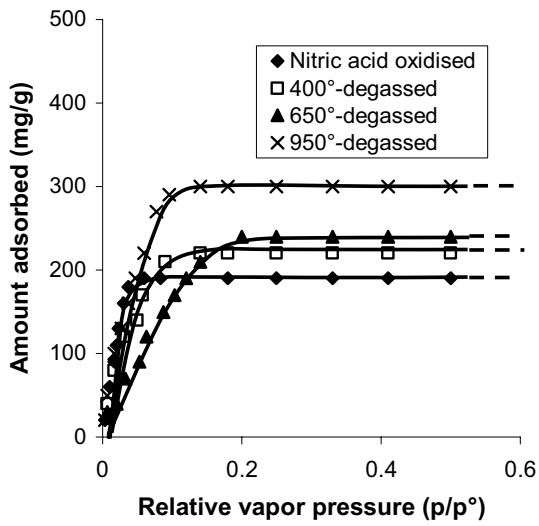

Fig. 6 Adsorption isotherms of carbondisulfide vapors on HNO_3-oxidised GAC-1240 sample before and after degassing

C. Adsorption Kinetics

The effect of time on the adsorption of CS_2 vapors by the activated carbon cloth sample at two different temperatures at a vapor pressure of 0.2 was determined. The adsorption was found to attain a constant value after a certain period of time. This is due to the fact that all the available sites become occupied at this point of time. The adsorption data was analysed using Empirical diffusion model and Linear driving force model.

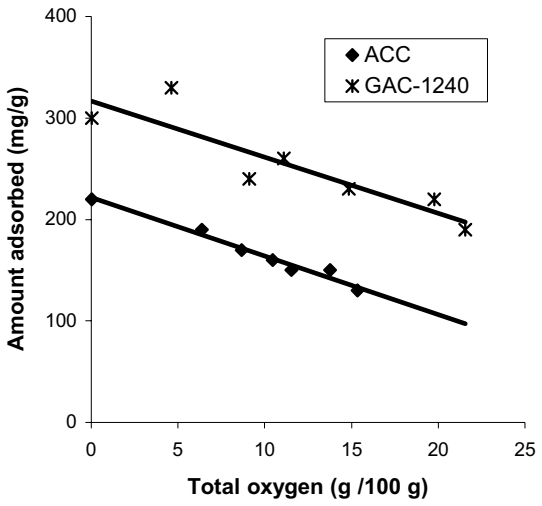

Fig. 7 Relationship between the maximum amount of carbondisulfide adsorbed and surface acidity of activated carbons

1) Empirical Diffusion Model

A simple empirical diffusion equation which is an alternative to Fickian diffusion equation [16] can be expressed as

$$\frac{M_t}{M_e} = kt^n$$

where M_t is the vapor uptake at time t, M_e is the equilibrium vapor uptake, K is adsorbate-adsorbent interaction coefficient, and n is the diffusional exponent. The values of n and K for the adsorption of CS_2 on as-received, oxidized and degassed ACC samples were calculated from the linear ln (M_t/M_e) against ln t plots and the values are recorded in Table III.

TABLE III
PARAMETERS OF EMPIRICAL DIFFUSION EQUATION FOR ADSORPTION OF CARBONDISULFIDE VAPORS ON DIFFERENT ACC SAMPLES

Carbon Sample	n	K
As -received	1.0	4.7×10^{-2}
HNO_3 -oxidised	0.93	4.0×10^{-2}
950°-degassed	1.06	5.0×10^{-2}

The values of the diffusion exponent (n) do not support the Fickian diffusion model, because for this model the value of n is generally less than 0.5 [17]. In the present case, however, the value of n is always greater than 0.5 and generally around unity in the case of all adsorbate-adsorbent combinations. This indicates that the adsorption of CS_2 does not involve Fickian diffusion but may be considered as a pseudo first order mass transfer process between the vapor phase and the adsorption sites. The values of interaction coefficient K have small values for all the three carbon samples indicating that CS_2 has little or no interaction with the oxygen surface groups.

2) Linear Driving Force Mass Transfer model (LDF)

The rate equation based on the LDF mass transfer model can be represented as:

$$\frac{M_t}{M_e} = 1 - e^{-kt}$$

where M_t and M_e are respectively the uptakes at any time t and at equilibrium and k is the rate constant. The kinetic data at temperatures of 303 and 313 K, when plotted with ln (1-M_t/M_e) versus time gave linear plots. The values of rate constants k_1 & k_2 at the two temperatures were determined and these have been used to calculate the activation energies of adsorption. The activation energy values for the adsorption of CS_2 are small and vary between 40-60 kJ/mol. This indicates the adsorption of CS_2 on activated carbons involves only physical forces

D. Isosteric Enthalpy of Adsorption:

The isosteric enthalpies of adsorption for CS_2 for the as-received, oxidized and degassed carbon cloth samples were calculated from the adsorption isotherms at two temperatures of 303 and 313 K using the integrated form of the Clausius-Clayperon equation.

$$\left(\ln\frac{p_1}{p_2}\right)_{n_a} = \frac{-\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

where p_1 and p_2 are the equilibrium vapor pressures of the adsorbate at temperatures T_1 and T_2 for a given amount adsorbed n_a, ΔH is the isosteric enthalpy of adsorption and R is the gas constant. The isosteric enthalpies of adsorption for different adsorbate-adsorbent systems are shown in Fig. 8.

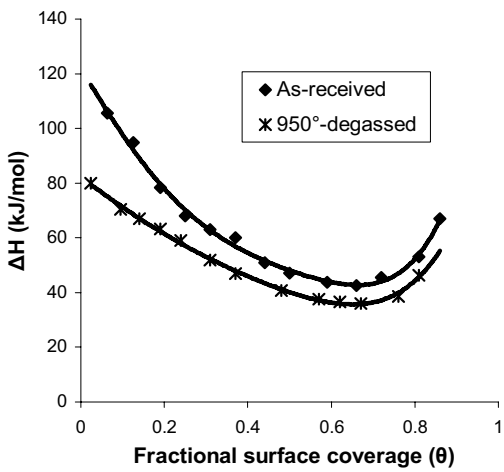

Fig. 8 Variation of isosteric enthalpy of adsorption with fractional surface coverage for the adsorption of carbondisulfide vapors on ACC

It is seen that the zero surface coverage isosteric enthalpy of adsorption for CS_2 is considerably larger on the as-received than that on the degassed carbon sample, the value varying between 85 and 122 kJ/mol. This can be attributed to the heterogeneous nature of the carbon surface in the case of the as-received carbon sample. This heterogeneity of the carbon surface is due to the presence of carbon – oxygen surface groups present at certain specific sites on the carbon surface. The 950°-degassed carbon sample is almost completely free of associated oxygen groups and therefore, has more or less a

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homogeneous surface. The enthalpy of adsorption decreases with increase in the surface coverage (θ) until θ = 0.6 and then increases. The decrease in ΔH is due to the decreasing effect of surface heterogeneity as the amount adsorbed increases. In addition, the lateral interactions are more or less absent in this range of surface coverage. At θ values greater than 0.6, the lateral interactions become more predominant resulting in an increase in ΔH above θ = 0.6.

E. Effect of metal impregnation

Activated carbon was impregnated with 0.18 % Cu, 0.36 % Cr and 1.6 % Ag. The adsorption isotherms of CS_2 on activated carbon cloth before and after impregnation are shown in Fig. 9.

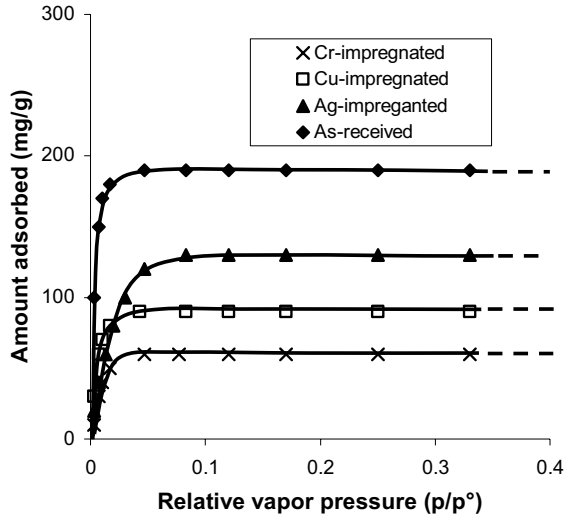
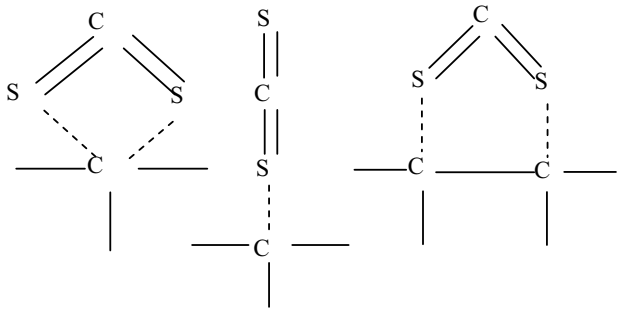


Fig. 9 Adsorption isotherms of carbondisulfide vapors on ACC sample before and after impregnation

It is seen that the impregnation results in a decrease in the adsorption of CS_2 vapors, the decrease being maximum for Cr impregnated and minimum for Ag impregnated carbon samples. The decrease in adsorption of CS_2 vapors on impregnation may be due to the fact that impregnation causes a partial blocking of the micropore entrances and thus reduces the available microporosity. The differences in the amount adsorbed by Cr, Cu and Ag impregnated activated carbon samples are attributed to the differences in the strengths of M-CS_2 coordination bonds in the surface complexes.

III. Mechanism Of Adsorption

It is apparent from the results presented above that the adsorption of CS_2 vapors is suppressed by the carbon- oxygen surface groups present on the carbon surface. The adsorption decreases when these surface groups are removed on degassing. This indicates that there is little interaction between the essentially nonpolar CS_2 molecules and the polar carbon-oxygen surface groups. Thus the adsorption of CS_2 vapors by carbons appears to involve hydrophobic interactions between the CS_2 and C-C layer planes of the carbons which may be represented as:



The magnitude of the low energy of activation indicates that there are no specific interactions between the CS_2 and carbon-oxygen groups. The formation of such C-S complexes has been suggested by [18].

IV. Conclusions

Adsorptive removal of CS_2 vapors by activated carbons depends on the surface area of the carbon and is influenced considerably by the carbon-oxygen surface groups. The adsorption is suppressed by the associated oxygen groups and increases when the associated oxygen group is eliminated by degassing. Thus oxygen-free activated carbons are better adsorbents for the adsorptive removal of CS_2 vapors from from working places of several industrial units and from the inhabited places.

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