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Adsorption of Chlorinated Hydrocarbon Pollutants on Silica Gel

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Abstract

A survey of indoor air pollutants was conducted. The removal of six chlorinated hydrocarbons, including methyl chloride, methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane, and tetrachloroethylene was performed using adsorption methods. The equilibrium uptakes of the six indoor pollutants on silica gel were determined gravimetrically at 25°C and at pressures up to saturation. The modified potential theory proposed by Dubinin and coworkers was used to correlate the adsorption data.

INTRODUCTION

Air pollution has traditionally meant pollution of the outdoor air-exhaust spewing from motor vehicles or smoke billowing from factories and refineries. Recently, however, studies have shown that indoor air is often dirtier than outdoor air. The Environmental Protection Agency (EPA) reported that toxic chemicals found in every home—from paint to cleaning solvents—are three times more likely to cause cancer than outdoor airborne pollutants, even in areas next to chemical plants (*1*). Since most people spend more than 60% of their time inside their homes and 20% of America's single-family homes could contain more cancer-causing gases than some people think is healthy, scientists are concerned that high indoor pollutant levels might have adverse health effects.

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Two factors that have aggravated the indoor-air problem are new chemical products and houses that are better insulated. Concern has also increased as researchers have learned more about the hazards of many of the chemicals that have long been in people's homes (*2*). A typical house harbors dozens of products that release organic chemicals. Many household-chemical products, such as spray paints, insecticides, and furniture polish, come in aerosol form. This causes tiny droplets of the product to be dispersed in the air and subsequently adds an additional chemical (the propellant) to those that are already present in the basic product. On the other hand, the nationwide drive to save energy by weatherproofing has made the air inside many homes and offices more polluted than the outside air.

CLASSIFICATIONS OF INDOOR AIR POLLUTANTS

The pollutants that pose the greatest threats inside homes and offices are not necessarily the same ones that pose the greatest problems outdoors. A summary of the sources with possible concentrations and threats of some indoor air pollutants is given in Table 1. As can be seen, there are a large variety of indoor air pollutants that pose a myriad of health threats to humans. Of all the indoor air pollutants, the chlorinated hydrocarbons, radon, formaldehyde, cigarette smoke, and unvented combustion products have drawn the most attention. The reason for concern about the chlorinated hydrocarbons, particularly methylene chloride, is that it is present in large amounts in several widely used consumer products. Each year approximately 135 million cans of paint stripper are used which contain from 50 to 80% methylene chloride. It has been estimated that three of every thousand who use a methylene chloride-based paint stripper no more than once per year between age 25 and 70 could develop cancer. Thus, methylene chloride is considered to pose the highest cancer risk of any household chemical.

REMOVAL OF INDOOR AIR POLLUTANTS

Indoor air pollution problems have just recently been brought to the attention of researchers, but most of the studies so far have focused only on determining the types and levels of the indoor air pollutants. Studies on the removal of indoor air pollutants are very limited and the results have not always been satisfactory. Complete removal of indoor air pollutants is a difficult task because of the diversity of the pollutants,

TABLE 1
Sources, Possible Concentrations, Indoor-to-Outdoor Concentration Ratios, and Threats of Some Indoor Air Pollutants

Pollutant	Sources of indoor pollution	Possible[a] concentration	I/O ratio	Threats (*3*)
Methylene chloride	Paint strippers and thinners	NA	>1	Nerve disorders, diabetes
Chloroform	Chlorine-treated water in hot showers	NA	>1	Anesthetic, eye irritation, cancer
Tetrachloroethylene	Dry-cleaning-fluid fumes on clothes	NA	>1	Nerve disorders, damage to liver and kidneys, possible cancer
1,1,1-Trichloroethane	Aerosol sprays	NA	>1	Dizziness, irregular breathing
Methyl chloride	Solvents, aerosol sprays	NA	>1	Nerve disorders, possible cancer
Carbon tetrachloride	Solvents, combustion	NA	>1	Headache, dizziness, cancer
Radon and progeny	Radioactive soil, groundwater, building materials	0.1–30 nCi/m^3	$\gg$1	Lung cancer
Formaldehyde	Insulation, particle board, furniture stuffing	0.05–1.0 ppm	>1	Irritation of eyes and throat
Carbon monoxide	Combustion equipment, engines, faulty furnaces, unvented gas stoves	100 ppm	$\gg$1	Headaches, irregular breathing
Nitrogen dioxide	Combustion, gas stoves, water heaters, dryers, cigarettes, engines	200–1000 μg/m^3	$\gg$1	Irritated lungs, children's colds
Benzo-*a*-pyrene	Wood stoves, tobacco smoke	NA	$\gg$1	Lung cancer
p-Dichlorobenzene	Air fresheners, mothball crystals	NA	>1	Cancer

(continued)

TABLE 1 (*continued*)

Pollutant	Sources of indoor pollution	Possible[a] concentration	I/O ratio	Threats (*3*)
Sulfur dioxide	Heating system	20 μg/m^3	<1	Choking, coughing, irritation of eyes and throat
Sulfate	Matches, gas stoves	5 μg/m^3	<1	Choking, chest pain, colds
Carbon dioxide	Combustion, humans, pets	3000 ppm	≫1	Irregular breathing
Ozone	Electric arcing	20 ppb	<1	Headache, coughing, chest pain, build-up of fluid in lungs
	UV light sources	200 ppb	>1	
Asbestos	Fireproofing	<1 fiber/cm^3	1	Lung cancer
Mineral and synthetic fibers	Products, clothes, rugs, wallboard	NA	—	Lung damage, cancer
Viable organisms	Humans, pets, rodents, insects, plants, fungi, humidifiers, air conditioners	NA	>1	Coughing, any kind of disease is possible
Respirable particles	Stoves, fireplaces, cigarettes, condensation of volatiles, resuspension, cooking, aerosol sprays	100–500 μg/m^3	≫1	Irritation of eyes, skin, and respiratory membranes, anesthetic, arrest respiration

[a] Concentrations listed are only illustrative of those reported indoors. NA = not appropriate to list a concentration.

many of which exhibit different properties and pose different health threats. The techniques developed so far for the removal of air pollutants have targeted a particular type of pollutant. For example, radon gas, toxic household chemicals, paint strippers, and combustion products can be directed away from the house by venting and then introducing fresh air into the home. Another method is to place filters in the forced-air heating or central air-conditioning systems to help in removing particulates and some organic pollutants. The techniques described above may be used to solve specific indoor air pollution problems, but only when the outdoor air is much cleaner than that which exists indoors. In view of the interest in using solar energy to heat and cool homes and offices, it may be feasible to use the same adsorbent found in solar cooling systems to also remove many indoor air pollutants. In this work a silica gel that has found use in dehumidification applications is evaluated as a possible candidate for adsorbing several chlorinated hydrocarbons from indoor air.

EXPERIMENTAL

The adsorbent used in this study was type PA40, 80-100 mesh silica gel supplied by Davison Chemical Co. All but one of the indoor chlorinated air pollutants given in Table 1 were investigated. These are methyl chloride, methylene chloride, chloroform, and carbon tetrachloride, which are a homologous series, and two other indoor air pollutants, 1,1,1-trichloroethane and tetrachloroethylene. All of the above chemicals were obtained from Fisher Scientific Co. and had purities greater than 99.5%.

The experimental adsorption studies were carried out gravimetrically using a Cahn R-2000 electrobalance housed in a vacuum bottle. The adsorption apparatus was designed such that either gases or vapors could be studied. The sample weight was monitored with a strip chart recorder connected to the electrobalance control unit. A refrigerated-heater bath with a copper circulation coil wrapped around the sample hangdown tube was used to control the adsorption temperature. A special vapor supply flask was used as the pollutant container. A vacuum system which consisted of two vacuum pumps, a sorption trap, and a diffusion pump was used to obtain a vacuum of 1×10^{-4} mmHg for the system. The leak rate of the complete system was approximately 0.005 mmHg/h. Two thermistor gauges were used to monitor the pressure when the system was evacuated and during adsorption runs. In addition, pressures up to 1 atm were measured with a Wallace and Tiernan absolute pressure gauge. A schematic diagram of the apparatus is shown in Fig. 1.

The electrobalance was calibrated to agree with the output signal of the recorder. The weight changes of the silica gel sample due to the adsorption of indoor air pollutants were detected by the electrobalance. The silica gel sample was regenerated by evacuating the system and applying heat at 423 K to the sample hangdown tube. Heating was continued until a constant sample weight was obtained. This typically

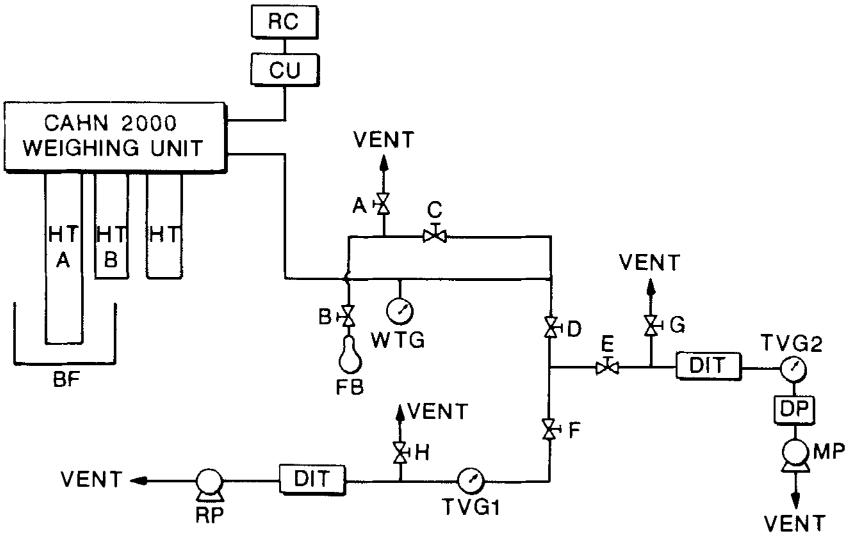

FIG. 1. Schematic diagram of adsorption apparatus.

A	Adjustable relief valve, ¼″	DP	Diffusion pump
B	Needle valve, ¼″	FB	Feed bottle
C	Bellows vacuum valve, ¼″	HT	Hangdown tube
D, E, F	Bellows vacuum valve, ½″	MP	Mechanical vacuum pump, holding pump
G, H	Needle valve, ¼″	RC	Recorder
BF	Constant temperature bath or furnace	RP	Mechanical vacuum pump, roughing pump
CU	Balance control unit	TVG	Thermistor vacuum gauge
DIT	Dry Ice trap	WTG	Wallace and Tiernan gauge

required from 4 to 10 h. Following regeneration, the adsorbent was cooled to the adsorption temperature and the adsorbate was introduced into the system. After equilibrium was reached, as indicated by a constant sample weight, the pressure and weight were recorded. Equilibrium isotherm data were taken from very low pressure up to saturation. Desorption measurements were made by reducing the system pressure.

ANALYSIS OF DATA

Adsorption isotherms were obtained from methyl chloride, methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane, and tetrachloroethylene on silica gel at 298 K after overnight regeneration of the adsorbent at 423 K *in vacuo*. The experimental equilibrium values are presented in Figs. 2 and 3. The maximum error introduced by the buoyancy effect on the adsorption measurements was evaluated and found to be less than 0.5%. Since this error was small, the buoyancy effect on the adsorption measurement was neglected. The weight of the sample was measured to within 10 μg with an error in the weight measurement of 0.0005%. Pressure was measured with an accuracy of ±0.15 mmHg. Except for the lowest pressures, the maximum error in pressure measurements was less than 0.3%. The average error over the entire adsorption range was estimated to be less than 1%. Several of the data points were reproduced with an error no greater than 1%.

The adsorption isotherms of all six indoor air pollutants on silica gel were Type I, according to the BDDT classification (*4*, *5*), and showed no apparent hysteresis when desorbing. The absence of capillary condensation, as noted from the equilibrium data, indicates that the silica gel contains mostly micropores. For a homologous series of chemicals, the amount of adsorbate removed by the silica gel increased as the molecular weight of the adsorbate increased as can be seen from Figs. 2 and 3. The fact that the maximum uptake of each adsorbate by the silica gel was in the range of 0.395–0.445 g adsorbate/g silica gel suggests that silica gel is an effective adsorbent for removing indoor air pollutants.

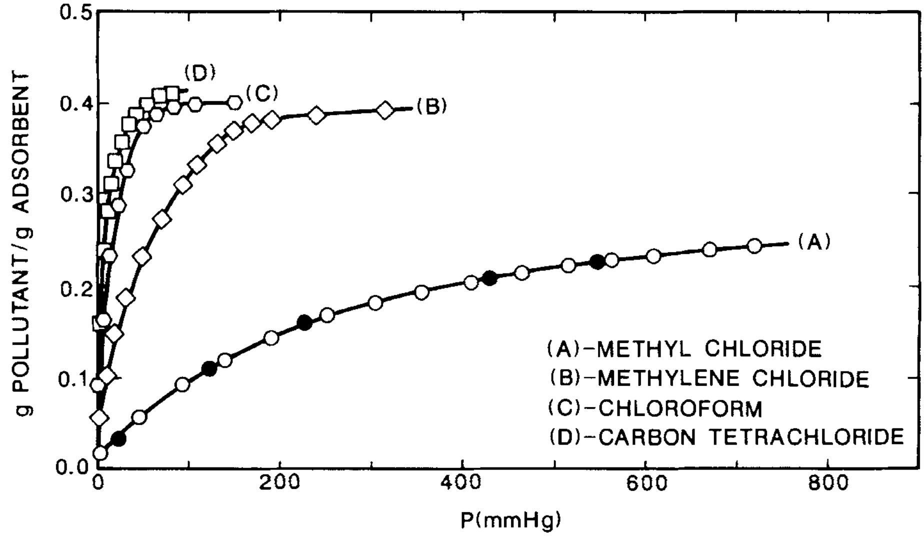

FIG. 2. Adsorption isotherms of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride on silica gel at 25°C. (Solid symbols represent desorption data.)

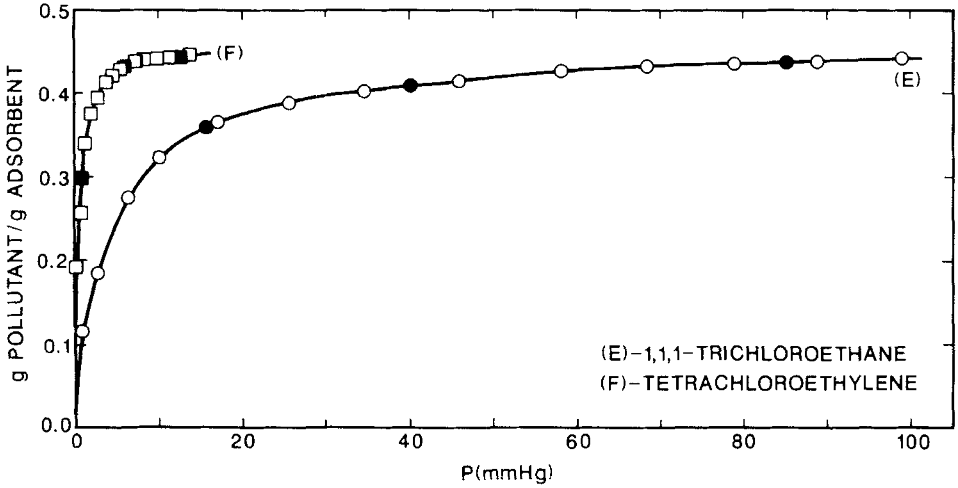

FIG. 3. Adsorption isotherms of 1,1,1-trichloroethane and tetrachloroethylene on silica gel at 25°C. (Solid symbols represent desorption data.)

The potential theory proposed by Polanyi (*6*, *7*) has been applied successfully for both monolayer and multilayer adsorption of gases and vapors on porous as well as nonporous adsorbents. The Polanyi theory in its original form assumes that the adsorbent exerts long-range attractive forces on the gas or vapor surrounding it. These forces give rise to a potential field with the potential decreasing as the distance from the adsorbent increases. The adsorption potential is described by

$$\varepsilon = RT \ln \left(\frac{P^s}{P} \right) \qquad (1)$$

where P^s is the saturation pressure of the vapor at system temperature, P is the pressure of the adsorption system, and R is the gas constant. Thus, a plot of the volume adsorbed versus the adsorption potential should yield a characteristic curve that is independent of temperature.

Dubinin (*8*) correlated equilibrium adsorption data for different gases and vapors on the same adsorbent by using a single characteristic curve. He suggested that for vapors of similar compounds, the adsorption potentials at equal adsorption volumes should have a constant ratio which is given by the ratio of the molar volumes of the adsorbed phases. Thus, a plot of the volume adsorbed versus the adsorption potential divided by the molar volume should yield a single characteristic curve for the adsorption of similar materials on the same adsorbent at different temperatures. The theory of pore filling proposed by Dubinin and coworkers (*9–11*) is particularly suited for describing the adsorption on microporous solids. As shown by Bering et al. (*10*), the volume adsorbed in the pores can be described by the expression

$$W = W_0 \exp\left[-\left(\frac{\varepsilon}{\beta E_0}\right)^m\right] \tag{2}$$

where E_0 is a constant characteristic energy of a standard adsorbate, β is the affinity coefficient, W_0 is the volume of adsorption space at saturation, and m is a constant. According to Eq. (2), a plot of $\ln W$ vs $(\varepsilon)^m$ should yield a straight line with a slope of $-(1/\beta E_0)^m$ and an intercept of W_0. If the adsorption of several compounds on one adsorbent can be described by Eq. (2) using only one value for the exponent m, then one of these isotherms may be used to predict the isotherms of the other compounds. By setting the affinity coefficient of the standard material equal to 1, which is methylene chloride in this study, the constants W_0 and E_0 can be determined from the standard isotherm. The affinity coefficient for other isotherms can be approximated by the ratio of the parachors as shown by Bering et al. (*9*).

The generalized correlation is presented in Fig. 4 according to the modified Polanyi theory. As noted, the experimental data can be approximated by a single characteristic curve. Because the generalized isotherm equation given by Eq. (2) contains three parameters, W_0, E_0, and m, the correlation of the data is possible if the parameter m is the same for all adsorbates on a single adsorbent. A value of 1.42 was found to produce the best least-squares fit to the data. The generalized equation obtained is

$$W = 0.301 \exp\left[-(\varepsilon/1.374\beta)^{1.42}\right] \tag{3}$$

The above equation was used to predict the adsorption equilibrium data for methyl chloride, methylene chloride, chloroform, and carbon tetrachloride using affinity coefficients of 0.95, 1.0, 1.15, and 1.30, respectively. The absolute percent deviation between the predicted and the experimental values is less than 10% except at pressure below 20 mmHg. It is interesting to note that values of m range from 1.2 to 1.8 for highly activated carbon and from 3.0 to 6.0 for zeolites. Dubinin (*8*) reported an m equal to 1.0 for one type of silica gel.

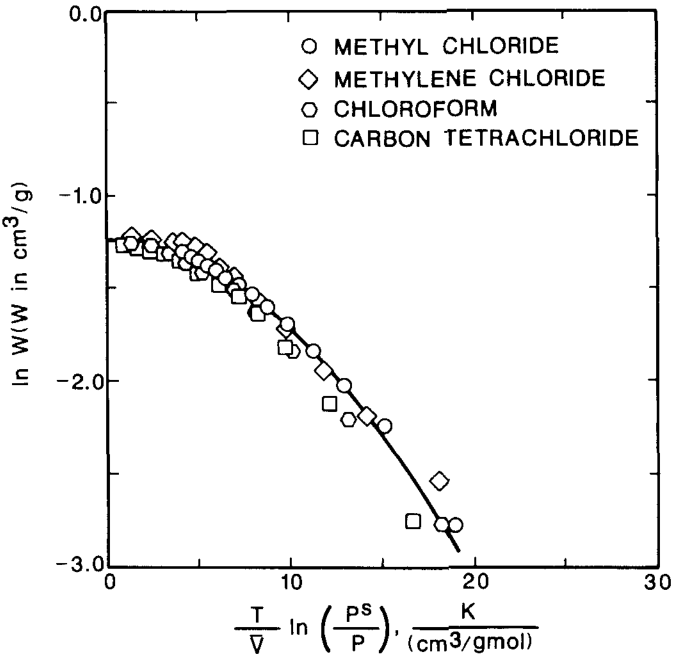

Fig. 4. Generalized adsorption correlation on silica gel.

CONCLUSION

A survey of indoor air pollutants was conducted. The removal of six pollutants (methyl chloride, methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane, and tetrachloroethylene) was investigated using adsorption methods. The adsorption isotherms of the six chlorinated hydrocarbons on silica gel were determined gravimetrically at 25°C and at pressures up to saturation. The generalized adsorption isotherm equation proposed by Dubinin and his coworkers was used to correlate the adsorption data. On the basis of this study, it is concluded that silica gel can be effectively used to both dehumidify as well as remove pollutants from indoor air.

SYMBOLS

E	constant characteristic energy
E_0	constant characteristic energy of a standard adsorbate

m	constant in the generalized isotherm equation
P	pressure
P^s	saturation pressure
R	gas constant
T	temperature
$\bar{V}$	molar volume of adsorbed phase
W	volume of adsorbed phase
W_0	volume adsorbed at saturation

Greek Letters

β	affinity coefficient, E/E_0
ε	adsorption potential

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