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DEVELOPMENT OF NOVEL SORBENTS FOR RESPIRATORS

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16. Abstract (Limit: 200 words) A study was undertaken of the effect of low volatility, nontoxic, organic dopants on the adsorption of low molecular weight polar organic vapors on activated carbon. The studies were made at 0% and 76% relative humidity. Calgon PCB 12x30 was the activated carbon used in the study. The dopants tested included glycerol, squalane, and 1-dodecanol. These organic compounds were chosen because of their extremely low vapor pressure, and low toxicity. A reduction was caused by the dopants in the amount of water vapor condensed in the micropores of the carbon. The modified activated carbon absorbed less of the low molecular weight polar organic when compared to the unmodified activated carbon. The proposed concept of producing a sorbent for respirators which is effective at removing a wide range of toxicants under a variety of relative humidity conditions by using a heavy organic dopant did not show promise for the systems and dopant levels studied.

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2. Modifying the activated carbon decreased the adsorption of the low molecular weight, polar, organic compounds used in this investigation.

ABSTRACT

The effect of low volatility, non-toxic, organic dopants on the adsorption of low molecular weight polar organic vapors on activated carbon was studied at 0 % and 76 % relative humidity. The dopants did cause a reduction in the amount of water vapor condensed in the micropores of the carbon. However, the modified activated carbon adsorbed less of the low molecular weight polar organic when compared to the unmodified activated carbon. Therefore, the proposed concept of producing a sorbent for respirators which is effective at removing a wide range of toxins under a variety of relative humidity conditions by using a heavy organic dopant did not show promise for the systems and dopant levels studied.

INTRODUCTION

The adsorbent in industrial respirator cartridges is activated carbon (either unimpregnated or impregnated with metals). At low relative humidities, water vapor has little effect on the adsorption of most organics in respirator cartridges. However at a critical relative humidity (often around 50 - 65 %), water can substantially reduce both the effective and equilibrium capacity for organics. This is due to capillary condensation of water in micropores in the activated carbon. In dry air, the cartridges are effective in removing nonpolar organic compounds with a molecular weight above 100. However, current chemical cartridges can be very ineffective at removing volatile, polar organics, such as ethylene oxide or vinyl chloride. A novel approach to increasing the efficiencies of current respirators under conditions of high relative humidity or in removing low-boiling, polar organics is investigated here.

In this work, a fraction of the pores in the activated carbon are filled with a low volatility, non-toxic, polar, organic liquid. The light, polar, organic vapor should dissolve in the heavy polar, organic liquid contained in these pores. The presence of the added organic liquid will not prevent the nonpolar or weakly polar organics in the air stream from adsorbing on the surface of the untreated carbon pores. If the heavy organic were not toxic and had a high odor threshold, the very small amount that would escape into the air stream would not harm or annoy the respirator user. The heavy organic liquid used to dope the activated carbon also could reduce the tendency of water to capillary condense in the adsorbent pores. This would lead to less reduction in capacity for toxic organics at high relative humidities. Development of a sorbent to solve either the problem of removal of toxic, volatile, polar organics or of decreased efficiency at high humidities would be an important advance. The solution of both problems in this work should result in the development of a "all purpose cartridge" that will provide protection against a wide range of toxic organic compounds at low or high relative humidities.

BACKGROUND

The effective adsorption capacity of activated carbon for organic vapors can be reduced substantially at high relative humidities for flow systems, such as respirator cartridges (1-7) or adsorber beds (8). However, at low relative humidities, water vapor has little effect. The critical relative humidity at which the water vapor effect becomes significant is about 50 to 65 %. In this same range of relative humidity, capillary condenstation of water in the carbon micropores also becomes significant (2,9-12). Organic adsorption in the water-filled pores is hindered, so that the equilibrium and effective adsorptive capacity of the carbon is reduced. However, the amount of condensed water depends on the contact angle between condensed water and solid carbon, and therefore on the amount and type of organic adsorbed.

Some toxic organics decompose upon exposure to wet carbon, resulting in an apparent increased lifetime for the cartridge at high relative humidities or carbon wetness (examples are formaldehyde (19) or sulfur dioxide (20)). These compounds represent a small minority of those industrial toxins of interest, and will not be further addressed.

It has been observed that the effective lifetime of a chemical cartridge decreases as the molecular weight of the organic adsorbate decreases, within a homologous series of compounds (13-15). Also, the adsorption of compounds having a high polarity tends to decrease the adsorbent lifetime. In fact, ethylene oxide, methylchloride, vinyl chloride, methanol, acetaldehyde -- all relatively common and toxic compounds -- have very short breakthrough times (13, 14). For example, the Mine Saftey Appliance Company (1988 catalog) sells a specialized system which would no be effective against chemicals other than that targeted. The very factor responsible for the effectiveness of unmodified activated carbon in removing nonpolar or slightly polar organics from air (viz., the hydrophobic surface) causes the carbon to be less effective in removing polar molecules. It is desirable to design an adsorbent that can effectively remove compounds having a wide range of polarities.

Novel Concept for Modifying Activated Carbon

It is proposed here that a certain fraction of the pores in the carbon be filled with a polar, organic compound having a very low vapor pressure, a high threshold limit value, and a high odor threshold. The low molecular weight, polar, organic components in the air stream would readily dissolve in this heavy polar, organic liquid. Nonpolar and weakly polar components would still be adsorbed on the surfaces of the unfilled pores. The very small amount of the heavy organic that would vaporize would be undetectable by the user and have no significant toxicity.

Exploitation of the concept of using a heavy, non-volatile organic in some of the pores, could lead to the design of a greatly improved cartridge adsorbent. It might be feared that properties of the smaller pores, in which the heavy organic would mainly reside, could be affected by dissolution of water in the organic condensate. However, this adverse effect might be minimized by careful choice of the condensed organic compound: in this study three heavy organics were studied.

Various techniques have been proposed for impregnating activated carbons to enhance their capacity to remove various classes of toxins or pollutants (16,17). In typical treatment methods, chemical substances are allowed to bind on the internal surfaces of the carbons, Providing the loci for the adsorption of particular classes of poisonous compounds. The use of metal salts to modify activated carbon is an excellent example of the ability of an impregnating substance to remove molecules that would otherwise only weakly adsorb. Unfortunately,the very sites that account for the enhanced adsorption of particular compounds may render the carbons more susceptible to the effects of high relative humidities.

The heavy organic dopant will adsorb to some extent on the carbon surface,even in those pores in which capillary condensation of the dopant does no occur. This will alter the wetting properties of the water on the carbon surface (as indicated by the contact angle between water and carbon). The higher the contact angle, the higher the minimum relative humidity at which capillary condensation of water into pores will occur. The adsorbed dopant organic layer on the carbon should make the carbon surface more hydrophobic,increasing the contact angle, thus decreasing the tendency for water condensation. Since water condensation is responsible for decreased respirator effectiveness at high relative humidities, a humidity resistant respirator cartridge could result from the use of the modified sorbent.

EXPERIMENTAL DESIGN AND METHODS

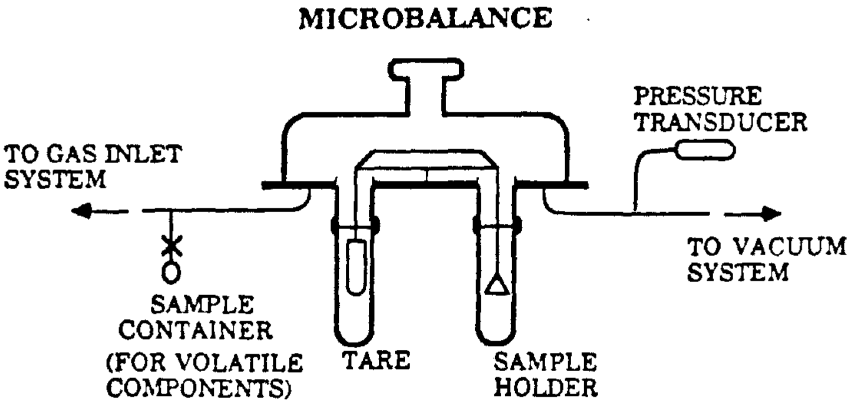
Preparation of Modified Carbon

The activated carbon used was Calgon PCB 12X30, a standard vapor phase carbon. Three heavy organic dopants used were: glycerol, squalane (2,6,10,15,19,23-hexamethyltetracosane), and 1-dodecanol. These dopants vary in polarity or hydrophilicity in the order: glycerol > 1-dodecanol > squalane, giving some indication of the influence of this parameter on the effectiveness of a given dopant. All three dopants have insignificant vapor pressure (boiling point from 259 to 350 C) and are not toxic (particularly in the extremely low vapor phase concentrations present from such involatile materials). In fact, glycerol is added to food as a sweetner and squalane is used as a skin lubricant in cosmetics.

Two methods were used to introduce the dopant into the pores of the carbon. First the dopant was dissolved in a 30/70 mixture of hexane and methanol and then added to the carbon and allowed to equilibrate overnight at 30 C in a temperature controlled water bath. The hexane - methanol mixture was removed by evacuating the sample. The temperature of the bath was elevated to 60 C and the modified carbon was placed under and ultralow vaccumn until the condensate formation in the cold finger ceased. The carbon was weighed to determine the increase in mass and it corresponded to the amount of nonvolatile organic dopant added to the carbon. The second method was the direct addition of the dopant to the carbon followed by annealing the sample at 100 C. The dispersal of the organic throughout the sample was uneven and not homogeneous. Evaluation of the dopants at elevated temperatures (150 -180 C) was not promising since one of the samples changed colors after only one week. Therefore, equilibrating the dopants with the carbon at a temperature above 100 C was not tried due to the apparent degradation of one of the dopants at elevated temperatures. All of the carbon used for these experiments was first boiled in distilled and deionized water and allowed to sit overnight and was then rinsed. The process was repeated three times. After the last rinse the carbon was allowed to drain several hours and was then vacuum dried until the condensate formation in the cold finger ceased. The cold finger was maintained at -20 C.

Measurement of Sorbent Capacities

The equilibrium adsorption of a toxic organic compound on modified and unmodified activated carbon was measured as a function of toxin partial pressure and relative humidity using a gravimetric adsorption apparatus as shown in the following diagram.



The apparatus employs a sensitive Cahn 1000 electrobalance, with connecting lines to vacuum, a highly-precise pressure transducer, and to a valving system for introducing toxic organic compounds into the system. In operation, the modified adsorbent is added to the container suspended from the micro balance; the system is evacuated until the pressure of residual gases or vapors is no greater than a few millitorr; and the starting pressure is read and recorded. With the main vacuum valve closed, measured quantities of the toxin were introduced through an extremely accurate chromatographic sampling valve which was calibrated by volume. The investigation of the effects of humidity on the adsorption capacity of the organic toxins were conducted by injecting 5.0 ml. of a saturated sodium chloride water solution through a septum located near the bottom of the tube encasing the the sample holder. The saturated sodium chloride solution maintains a constant 76 % relative humidity as long as the solution is in equilibrium with sodium chloride crystals. The vaporization of water when the saturated sodium chloride solution was introduced into the evacuated system left a surplus of sodium chloride crystals equilibrated with the remaining liquid water in the system at the base of the tube. A thermometer was also located in the same tube so that the temperature of the system was monitored. Temperature control was not a problem since the research facility is located underground and is not subject to wide temperature variations.

Significant problems were encountered with this apparatus. The organic toxins selected for this investigation solubilized in the polymer holding the armature (electromotive portion of the balance) together. The armature suffered a catastrophic failure and the entire Cahn 1000 balance was returned to the manufacturer for repair. The new armature also interacted with the toxins but to a lesser extent since the manufacturer changed to a more inert polymer system. Due to the solubilization of the toxin into the armature polymer it usually required 24 to 48 hrs to obtain a 50 millitorr pressure readings. A weighted amount of carbon was then loaded on the sample holder of the balance and the system was evacuated for another 24 hours. The difference in weight of the carbon, before and after the 24 hours decreased by a maximum of only two percent. The humidity studies required another 24 hours of equilibration time before the introduction of the organic toxin. The equilibration time was determined by monitoring the weight change as a function of time. Equilibrium is defined as no measurable change in weight for five minutes.

Special care was required for the acetaldehyde. Due to the high vapor pressure the solution and injection syringe required refrigeration below zero degrees celsius. Any attempt to draw the organic solution into the syringe at room temperature would vaporize the solution. The valve loop was filled and flushed three times to cool the loop before the final loading and injection into the system.

RESULTS

The adsorption of water on carbon modified with squalane and unmodified carbon is shown in Figure 1. The adsorption of propylene oxide on carbon modified with squalane and unmodified carbon at zero percent relative humidity is shown in Figure 2. The adsorption of propylene oxide on carbon modified with squalane and unmodified carbon at 76 % humidity is shown in Figure 3. The adsorption of acetaldehyde on carbon modified with squalaneand unmodified carbon at 76% humidity is shown in Figure 4. The adsorption of carbon tetrachloride on unmodified carbon and modified carbon with squalane, glycerol, and dodecanol at 76 % humidity is shown in Figure 5.

DISCUSSION

The effect of modifying the carbon with squalane on water vapor adsorption is illustrated in Figure 1. The three curves show the adsorption of water decreases as the squalane loading increases. The minimum adsorption of water vapor occurred on carbon loaded with 10 % squalane and the maximum adsorption occurred on the unmodified carbon. This indicates that the heavy organic is in the pores of the carbon and preventing the water vapor from condensing in those pores. This is a very positive outcome and a desired result for this investigation.

The adsorption of propylene oxide on unmodified and squalane modified carbon at zero percent humidity is shown in Figure 2. The three curves show the adsorption of propylene oxide decreases as the squalane loading increases. The adsorption of propylene oxide on the carbon modified by 10 % squalane is substantially less than the unmodified carbon. This indicates that the dopant and the toxin are competing for the same adsorption sites and that the solubilization of the toxin in the heavy organic is not significant enough to offset the adsorption sites occupied by the heavy organic that would otherwise been available for the toxin.

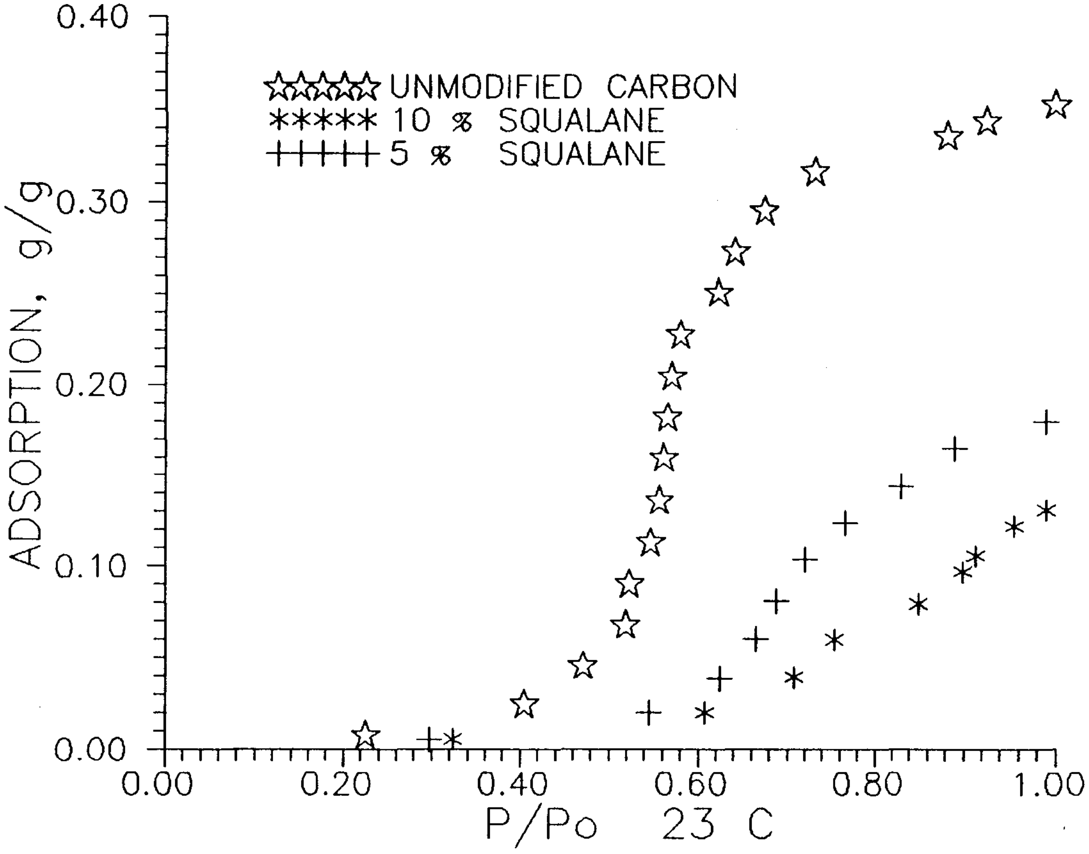


FIGURE 1: ADSORPTION OF WATER VAPOR ON MODIFIED AND UNMODIFIED CARBON

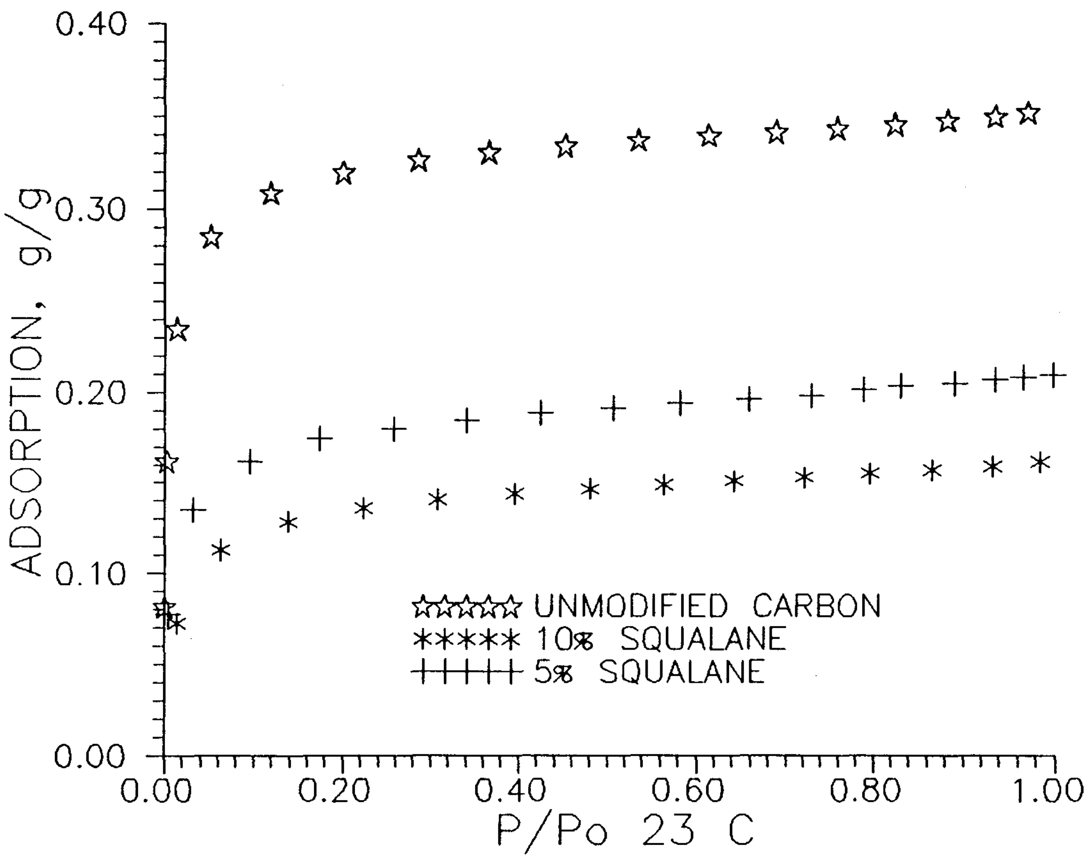


FIGURE 2: RELATIVE ADSORPTION OF PROPYLENE OXIDE ON MODIFIED AND UNMODIFIED CARBON AT ZERO PERCENT RELATIVE HUMIDITY

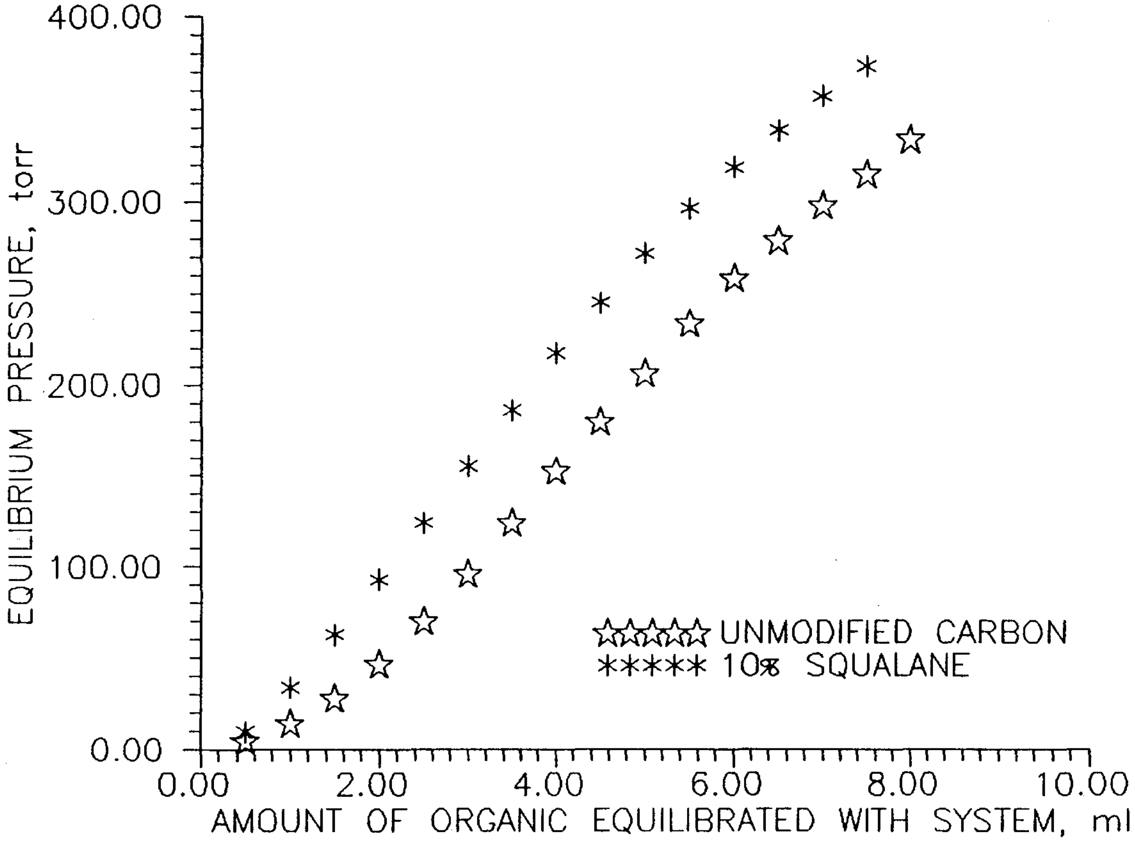
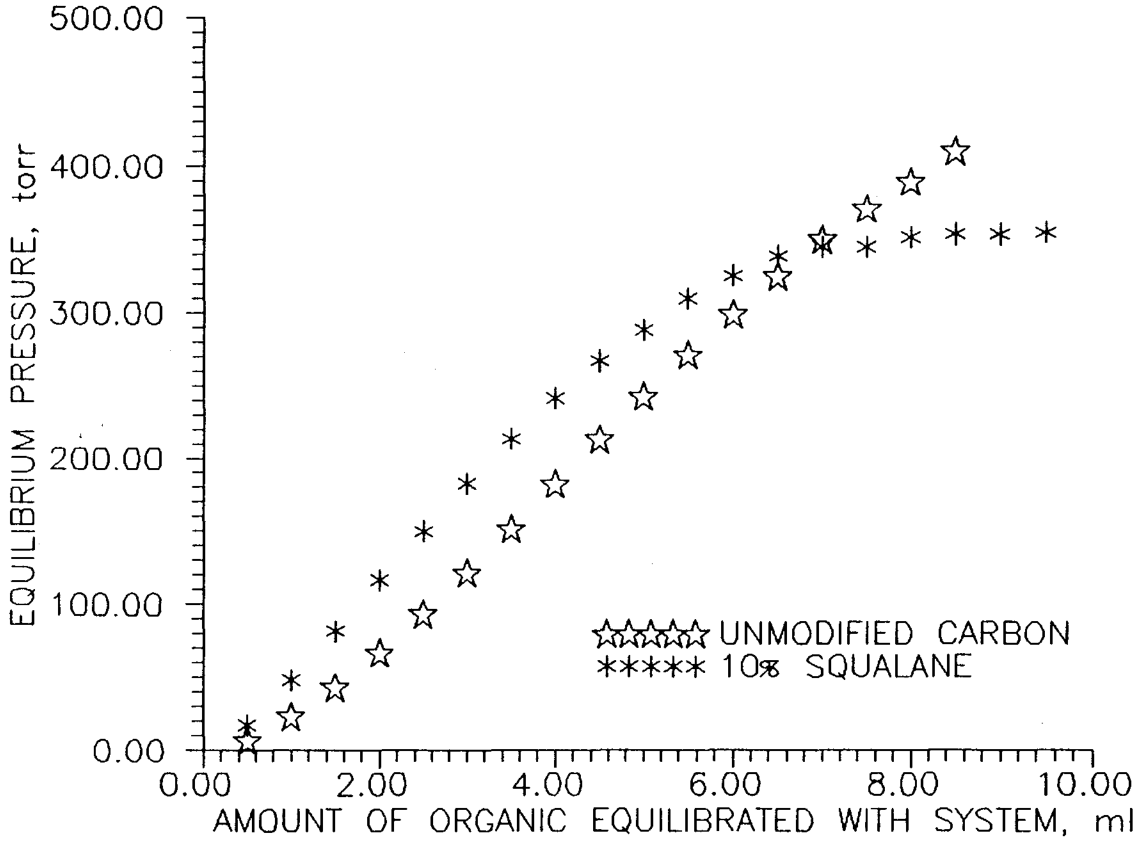


FIGURE 3: RELATIVE ADSORPTION OF PROPYLENE OXIDE ON MODIFIED AND UNMODIFIED CARBON AT 76% RELATIVE HUMIDITY



FIGRUE 4: RELATIVE ADSORPTION OF ACETALDEHYDE ON MODIFIED AND UNMODIFIED CARBON AT 76% RELATIVE HUMIDITY

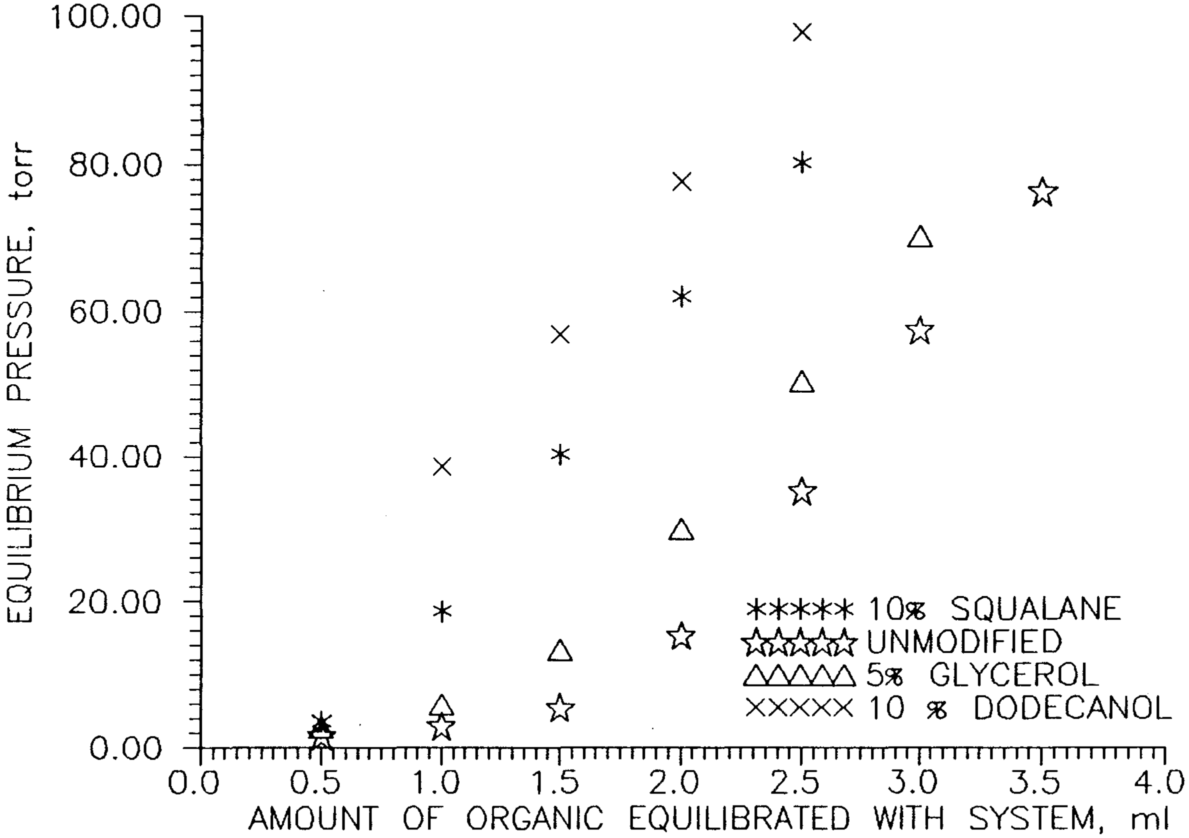


FIGURE 5: RELATIVE ADSORPTION OF CARBON TETRACHLORIDE ON MODIFIED AND UNMODIFIED CARBON AT 76% HUMIDITY

The adsorption of propylene oxide on unmodified and squalane modified carbon at 76 % relative humidity is shown in Figure 3. The adsorption is inferred by pressure change. In previous plots the actual adsorption was weighed and the equilibrium pressure was measured. However, the actual adsorption on the carbon and the solubilization into the armature are indistinguishable for the organic toxin in the presence of 76 % humidity. The reason for this is that there is displacement of water from the surface of the carbon as the toxin adsorbs on the carbon. Therefore direct weight of the toxin is not possible. The decrease in pressure is due to both the adsorption of the toxin on the carbon and on the armature polymer and therefore cannot yield an absolute adsorption value for the toxin on the activated carbon. However, the data presented here assumes that the adsorption on the armature is the same from one experiment to the next. Therefore, for a given volume of toxin introduced into the system, the higher the equilibrium pressure the less adsorption of the toxin on the carbon. The comparison of equilibrium pressures for the modified and unmodified carbon in Figure 3 shows that for a given volume of toxic organic the modified carbon equilibrates at higher equilibrium pressures than the unmodified carbon. In essence there is less adsorption of the toxin on the modified carbon as compared to the unmodified carbon. Therefore, the trend illustrated in Figure 2 is also followed at elevated humidities. These results do not support the use of this particular modified carbon with this particular toxin.

The adsorption of acetaldehyde on unmodified and squalane modified carbon at 76 % relative humidity is shown in Figure 4. Acetaldehyde shows the same characteristics as propylene oxide under the same experimental conditions. Acetaldehyde equilibrates at higher equilibrium pressures for the modified carbon when compared to the unmodified carbon. These results do not support the use of this particular modified carbon with this particular toxin.

The adsorption of carbon tetrachloride on unmodified carbon and modified carbon at 76 % relative humidity is shown in Figure 5. The carbon was modified with sqaulane, glycerol and dodecanol. The equilibrium pressures of the toxin were all higher for the modified carbons when compared to the unmodified carbon. This can only be interpreted as there being lower adsorption of the toxin on the modified carbon as compared to the unmodified carbon. Therefore, these results do not support the practical use of these particular modified carbons with this particular toxin.

CONCLUSIONS

The adsorption of water on the modified carbon was significantly less than on the unmodified carbon. However, there was no toxin-dopant system that showed the necessary synergism desired. The toxins adsorbed less on the modified carbon at zero and 76 % relative humidity than on the unmodified carbon. Therefore, there is no data indicating that heavy polar organic dopants improve the adsorption of low molecular weight polar organic compounds on activated carbon at zero or 76 % relative humidity.

REFERENCES

1. Nelson, G.O., and Correia, A.N., Am. Ind. Hyg. Assoc. J., **37**, 514 (1976).

2. Nelson, G.O., Correia, A.N., and Harder, C.A., Am. Ind. Hyg. Assoc. J., **37**, 280 (1976).

3. Nelson, G.O., and Harder, C.A., Am. Ind. Hyg. Assoc. J., **37**, 205 (1976).

4. Henry, N.W., Wilhelme, M.S., and Wilhelme, R.S., Am. Ind. Hyg. Assoc. J., **40**, 1017 (1979).

5. Ackley, M.W., Am. Ind. Hyg. Assoc. J., **48**, 447 (1987).

6. Stampfer, J.F., Am. Ind. Hyg. Assoc. J., **43**, 319 (1982).

7. Moyer, E.S., Am. Ind. Hyg. Assoc. J., **44**, 46 (1983).

8. Scamehorn, J.F., Ind. Eng. Chem. Process Des. Dev., **18**, 210 (1979).

9. Okayaki, M., Tamon, H., and Toei, R., J. Chem. Eng. Japan, **11**, 209 (1978).

10. Christian, S.D., and Tucker, E.E., Am. Lab., **13**(9), 42 (1981).

11. Christian, S.D., and Tucker, E.E., Am. Lab., **13**(10), 47 (1981).

12. De Boer, J.H., Lippens, B.C., Linsen, B.G., Broekhoff, J.C.P., van den heuvel, A., and Osinga, Th.J., J. Colloid Interface Sci., **21**, 405 (1966).

13. Nelson, G.O., and Harder, C.A., Am. Ind. Hyg. Assoc. J., **35**, 391 (1974).

14. Freedman, R.W., Ferber, B.I., and Hartstein, A.M., Am. Ind. Hyg. Assoc. J., **34**, 55 (1973).

15. Moyer, E.S., Am. Ind. Hyg. Assoc. J., **48**, 791 (1987).

16. Asakawa, T., Ogino, K., and Yamabe, K., Bull. Chem. Soc. Japan, **58**, 2009 (1985).

17. Lin, P.J., and Parcher, J.F., J. Colloid Interface Sci., **91**, 1 (1983).

18. Breysse, P.N., White, N., Ryan, C.M., and Corn, M., Am. Ind. Hyg. Assoc. J., **44**, 762 (1983).

19. Henry, N.W., Am. Ind. Hyg. Assoc. J., **42**, 853 (1981).

20. Ackley, M.W., Am. Ind. Hyg. Assoc. J., **46**, 679 (1985).