Activated Carbon Fibers For the Removal of Chemical Warfare Simulants

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Removal of chemical warfare agents such as dimethylmethylphosphonate (DMMP), carbon tetrachloride, and chloropirinic vapor were carried out on activated carbon fibers, and compare the removal efficiency with those of metal-impregnated activated carbon and carbon deposited cloths at various conditions. The vapors were passed through the carbon adsorbent packed bed at constant flow rate. The vapor concentrations in influent and effluent air were measured by gas chromatography. The adsorption amount of DMMP on activated carbon fiber was 0.585 g/g-ACF, which was 7.4 times larger than that of metal-impregnated activated carbon at the breakthrough point (0.004 mg/l). DMMP was physically adsorbed on ACF. The ACF saturated with DMMP was completely regenerated at 121°C, 1.2 atm, 30 min. The adsorption amounts of carbon tetrachloride and chloropirinic on ACFs were 7.7 and 18 times larger than that of metal-impregnated activated carbon at the breakthrough point.

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1. Introduction

In many industrial sites, several types of respirator were developed and employed for protection people from vapor type contaminants depending on contaminant species. Generally, the capability of respirator is dependent on the canister, which includes adsorbent against contaminants. DMMP [dimethyl methyl-phosphinate, CH₃P(O)(OCH₃)_2], IMPE (isopropyl methylphosphonito floriate), carbon tetrachloride (CCL₄) and chloropirinic (PS gas, CCL₃NO₂) are using as simulants for chemical warfare agents. Up to now, many researchers have attempted to characterize activated carbons. Especially, metal-impregnated activated carbon is using to remove toxic gases such as nerve agent from air. However, granular activated carbon (GAC) is particularly disadvantageous for gas mask due to its slower adsorption kinetics and a pore surface chemistry which is acidic in nature (many chemical warfare gases are acidic or breakdown into acidic components). Therefore, the use of fiber system with basic pores should greatly enhance adsorption efficiency. In addition, macro- and mesopore populations which dominate GAC surfaces hold adsorbents weakly as compared to the micropores. Activated carbon fiber (ACF) is a fibrous microporous carbon adsorbent, which has larger surface area, lower diffusional resistance and pressure drop than activated carbons. ACF has shown far better adsorption capacity of DMMP than metal-impregnated activated carbon. Phosgene is a highly toxic gas and prepared from carbon tetrachloride. Many researches have been performed to remove these toxic gases from air by activated carbon. However, there are few reports for the adsorption of these vapors by activated carbon fibers. In this study, adsorption and desorption of DMMP, carbon tetrachloride, and chloropirinic vapor were investigated on activated carbon fiber, and compared the removal efficiency with those of metal-impregnated activated carbon and activated carbon deposited cloths.

2. Experimental

Liquid DMMP (97%, Aldrich), carbon tetrachloride, and chloropirinic contained in a bubbler were placed in a temperature controlled water bath to maintain constant vapor pressure. Dried air was supplied from the air reservoir to the bubbler at the rate of 1.0 l/min. Each vapor was generated by air bubbling and flowed into the glass column. The column (ID: 1.2 cm, L: 1500 m²/g, Osaka gas Co., packing height = 2 cm, packing density = 0.035 g/cm³), ASC-AC (AgNO₃: 0.1–1.5%, Cu: 8.5%, CrO₃: 3.5% impregnated activated carbon, 12 × 30 mesh grade VI, 850 m²/g, Calgon Co., packing density = 0.63 g/cm³), and ACF–deposited cloth (I, II) respectively. All the lines from bubbler to GC analyzer were wrapped with heat band to prevent condensation of vapors. The vapor concentrations of influent and effluent were continuously measured with GC (HP–5890). The breakthrough time was denoted as the time when the effluent vapor concentration reached to 0.004 mg/l for DMMP, and 0.005 mg/l for carbon tetrachloride and chloropirinic. TGA/DTA investigation was performed to characterize carbon adsorbents and determine the proper desorption temperature. Desorption of DMMP and other vapors from carbon adsorbents were carried out in autoclave at 121°C, 1.2 atm, 30 min. Adsorption capacities of the regenerated ACFs for the vapors were investigated and compared with those of original ACF and regenerated ASC–AC.

3. Results and discussion

Figure 1 shows the breakthrough curves of DMMP from
the carbon adsorbent bed (0.08 g ACF, 0.8 g ASC-AC) for the influent concentration of 0.52 mg/l. The curve of ACF was very steep just after the breakthrough time (t_b), which means that the mass transfer zone of ACF was very narrow relative to the bed height because of surface micropores and most of adsorption capacity of ACF was consumed. A narrow mass transfer zone is desirable to make efficient use of the adsorbent and to reduce the energy costs in regeneration.\(^9\) The breakthrough curve of the ASC-AC was typically extended and showed less efficient in the adsorption capacity than ACF. The breakthrough times of ACF and ASC-AC were 90 and 120 min., respectively. The adsorption amounts of DMMP at the breakthrough time were 0.59 g/g-ACF and 0.08 g/g-ASC-AC. The maximum adsorption capacity can be obtained from mass flow rate and operation time. The ratio of the breakthrough time to the half time (C/C_0 = 0.5) represents the removal efficiency of the carbon adsorbent packed bed.\(^6\) In this experiment, the efficiency of ACF packed bed was 71 %, while that of ASC-AC was only 32% for the removal of DMMP.

**Figure 2** shows breakthrough curves of DMMP on ACF at different influent concentration. The breakthrough time and the removal efficiency decreased as the increase of influent concentration. However, the adsorbed amount of DMMP at the breakthrough time increased in proportion to the influent concentration. The adsorbed amounts of DMMP at the break point for influent concentration of 0.52, 0.78, 1.17, and 2.55 mg/l were 0.59, 0.78, 0.86, and 1.12 g/g-ACF, respectively.

**Figure 3** shows the TGA/DTA curves of (a) ASC-AC, (b) ACF, (c) DMMP saturated ASC-AC, and (d) DMMP saturated ACF in air. For ASC-AC, there was a moisture vaporization up to 105°C, a small weight loss was observed up to 278 °C, then sudden decomposition was happened showing sharp exothermic peak at the temperature 278.3°C, which indicated that a catalytic reaction occurred between carbon and the impregnated metals. For ACF, there was a very small

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**Fig. 2.** Breakthrough curves of DMMP at different influent concentration.

**Fig. 3.** TGA/DTA curves of (a) ASC-AC, (b) ACF, (c) DMMP saturated ASC-AC, and (d) DMMP saturated ACF in air.
moisture vaporization up to 100°C and only a small amount of weight loss was observed up to 498°C, then followed rapid decomposition showing that of typical carbon fiber. For DMMP saturated ASC-AC, the vaporization curve was different from that of ASC-AC, showing that DMMP was moisture soluble. There was also sudden decomposition at 283.5°C showing the catalytic reaction. For DMMP saturated ACF, DMMP did not evaporated from the ACF up to 100°C. Desorption started above 100°C, remarkably progressed after 120°C, and continued up to 318°C. The amount of weight loss from DMMP-saturated ACF was the same as the amount of DMMP adsorbed in ACF. This means that the DMMP was only physically adsorbed on ACF.

Figure 4 and Fig. 5 show the breakthrough curves of DMMP on regenerated ACFs and regenerated ASC-AC at the same conditions. All the regenerated ACFs showed the same adsorption capacities to that of original ACF. On the other hand, the ASC-AC saturated with DMMP was not completely regenerated at 121°C, 1.2 atm, 30 min., and showed about 60% to original ASC-AC in the adsorption capacity at the breakthrough time.

Figure 6 shows the breakthrough curves of carbon tetrachloride on ACF (0.54 g), ASC-AC (7.0 g), and AC-deposited cloth (I) (1.39 g) at 7.0 mg/l, 0.61/min., 25°C. The breakthrough curves for ACF and AC-deposited cloth (I) were very steep just after the break point, which means the mass transfer zones of ACF and AC-deposited cloth were narrow relative to the bed height and most of adsorption capacity was utilized. However, the adsorption amount of carbon tetrachloride on AC-deposited cloth was far lower than that of ACF. The breakthrough curve of ASC-AC was typically extended and showed less efficient the adsorption amount than ACF. The adsorption amounts of carbon tetrachloride on ACF, ASC-AC, and AC-deposited cloth were 0.194 g/g-ACF, 0.013 g/g-ASC-AC and 0.021 g/g-AC-AC, respectively at the break point (C = 0.005 mg/l).

Figure 7 shows the breakthrough curves of carbon tetrachloride on ACF for different packing heights. The adsorption amounts of given height at the break point in this experiment were 0.117, 0.175, 0.194, 0.204, and 0.21 g/g-ACF, respectively. The adsorption amount increased as the increase of packing height, because the decrease of unused packing height.

Figure 8 shows the breakthrough curves of PS on ACF, AC-deposited cloth (I), (II), and ASC-AC for different packing heights at 7.0 mg/l, 0.41/min., 25°C. The breakthrough time of ACF was longer than other carbon adsorbents in spite of smallest packing amount.

Figure 9 shows the breakthrough curves of PS on ACF for different packing height at 7.0 mg/l, 0.41/min., 25°C. The adsorption amounts of given heights at the breakthrough time in this experiment were 0.389, 0.428 and 0.519 g/g-ACF, respec-
Fig. 8. Breakthrough curves of PS on carbon adsorbents at 7.0 mg/l, 0.41/min.

Fig. 9. Breakthrough curves of PS on ACF at various packing heights.

atively. The adsorption amount of PS increased as the increase of packing height, because the decrease of unused packing bed.

4. Conclusion

Adsorption of DMMP, carbon tetrachloride, and chloropicrin vapors were effectively achieved by activated carbon fiber showing narrow mass transfer zone. The adsorption capacity of activated carbon fiber was 7.4 times higher for DMMP, 7.7 times higher for carbon tetrachloride, and 18 times higher for chloropicrin than that of conventional metal-impregnated activated carbon (ASC–AC) at the breakthrough point of 0.004 mg/l because of uniformly developed micropores and higher specific surface area. The adsorption capacity of vapors increased with the increase of influent concentration, packing height, and lower flow rate of vapors. The vapors were physically adsorbed on ACFs. Evaporation of DMMP from ACF progressed above 100°C. Regeneration of DMMP saturated ACFs was completely performed at 121 °C, 1.2 atm, 30 min, while ASC–AC showed only 60% regeneration at this conditions. ACF can be used as an effective adsorbent for the removal of toxic gases, especially for chemical warfare simulants.

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References

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