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Removal of NO using surface modified activated carbon fiber (ACF) by impregnation and heat-treatment of propellant waste

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Abstract−The surface of activated carbon fiber was modified by impregnation and heat-treatment of propellant waste to introduce nitrogen functional groups such as pyridines, pyridones and pyrrols. The pore structure and specific surface area of those modified ACFs were slightly changed; however, the NO removal capacity of the surface modified ACF by propellant waste increased about twice that of the as-received ACF due to the addition of chemical adsorption by nitrogen functional groups. Propellant waste can be used as an ACF surface modifier for the removal of NOx.

Key words: Activated Carbon Fiber, Surface Treatment, Propellant, Adsorption, NO Removal

INTRODUCTION

Porous carbons have been widely used as adsorbents, catalyst/catalyst supports and energy storage materials due to their high surface area and large pore volume [1]. Activated carbon fiber (ACF) as a novel porous carbon with various shapes (cloth, paper, monoliths and felt) has narrower pore distribution and the micro-pore opening is located on the external surface of fiber. Therefore, it displays faster adsorption dynamics than commercial activated carbons because it shortens the molecular diffusion path inside the fiber [2]. ACF is thought as an excellent adsorbent for solvent recovery, water purification, environmental protection and energy storage [3-5].

Both the pore structure and surface functional groups of ACF have influenced its adsorption capacity, catalytic activity or catalyst support performance. The nitrogen functional groups such as pyridines, pyridones and pyrrols on the surface of ACF take a role in its applications [6-8]. The nitrogen atoms on the ACF surface could be introduced through physical and chemical approaches, such as impregnation of urea [7], reaction of CN [9], nitrogen plasma treatment [10], etc.

Solid propellants for guns, artillery, and mortars are low-explosive materials designed to burn at a controlled rate and rapidly produce gases that create the pressure to accelerate projectiles toward targets [11,12]. Propellants consisting of nitric esters such as nitrocellulose (NC) inherently have chemical instability due to the low bonding energy (155 kJ/mol) of the nitric ester group CH_2-O-NO_2 [13]. Disposal of solid propellant wastes has been a simple task in the past. Materials were placed in an open area and ignited from a remote site. However, problems about open burning of propellants increased with concerns about air quality lately. The Environmental Protection Agency (EPA) and local agencies such as the Bay Area Air Quality Management District (BAAQMD) increased the attention given to open burning of all kinds [14].

Propellant waste that contains nitric ester can be used as a source material of nitrogen functional groups on carbon. However, until now there has been no report about the introduction of nitrogen functional groups on the carbon surface by propellant waste heat-treatment.

In this study, a propellant waste dissolved solution was impregnated on the surface of ACFs and these ACFs were heat-treated to obtain newly developed nitrogen functional groups. The surface modified ACFs were characterized and their NO removal capacities were investigated.

EXPERIMENTAL

1. Surface Modification of ACF

The materials used in this experiment were activated carbon fiber tow (Toyobo, KF-1000, 1,000 m^2/g) and nitrocellulose based propellant. The propellant was manufactured by Han-Wha Co. (Korea) 20 years ago and now it is regarded as a propellant waste due to its low stability.

ACF tow was cut down to 2 cm, washed and dried at 120 °C for 2 hr to remove moisture and adsorptive. The ACF was put into propellant waste dissolved ethylacetate solution to impregnate propellant. The concentration of propellant was adjusted to 1, 5 and 10 wt%. The propellant-impregnated ACFs were dried and heated to 500 °C to introduce nitrogen functional groups on ACF surface. The as-received and modified ACFs were labeled as K-0-0, K-1-500, K-5-500, and K-10-500 according to the propellant concentration and heat treatment temperature.

2. Characterization

The nitrogen adsorption isotherms of modified ACF were measured by BET apparatus (Micromeritics ASAP 2000) at 77.4 K in the range of relative pressure from $10^{-}6$ to 1. All samples were outgassed at 300 °C for overnight before the measurement. The specific surface area (S_{BET}) was calculated by means of the BET equation. The total pore volume (V_{Total}) was estimated to be the liquid volume of N_2 at 0.995 of relative pressure. The micropore volume ($V_{Micropore}$) was calculated by using a DR equation.

Thermal gravimetric analysis (TGA) was operated in the atmosphere at 20-780 °C with a heating rate of 10 °C/min by TGA 2050 (TA Instrument, USA)

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Elemental analysis was performed to study the nitrogen, carbon, hydrogen and oxygen contents (Flash EA 1112 series of Thermo Fisher Scientific).

The functional groups of ACF surface were investigated by X-ray photoelectron spectroscopy (XPS, MultiLab 2000 spectrometer Thermo electron corporation, England). The survey spectra were collected from the binding energy of 0-1,100 eV with a step size of 0.5 eV. The high-resolution spectra of N1s were acquired over 390-410 eV with a step size of 50 meV [15].

The SEM images of samples were observed through scanning electron microscopy (Topcon, SM-500, Japan) operated at 20 kV and 15 mA to study morphologies of ACFs. Before observation, the samples were sputtered with gold for 2 min in order to avoid charging.

NO removal was performed with a fixed bed flow reactor maintained at 30 °C. 1 g ACF was packed in glass tube of 25 mm diameter and packing height was 50 mm (ρ=0.04 g/cm^3). The concentration of NO in model gas was 900 ppm and the flow rate was 500 ml/min. The concentrations of the NO and NOx at the outlet were detected with the NO/NOx analyzer (ULTRAMAT 23, Siemens).

RESULTS AND DISCUSSION

1. Characterization of Pore Structures

Structural characteristics of ACFs are listed in Table 1. The specific surface area and total pore volume decreased, while the average pore size increased with the increase of propellant concentration. This indicates that entrances of ACF were blocked by newly developed nitrogen groups, which was similar to the results of other researchers [3,16].

Fig. 1 shows the nitrogen adsorption isotherms and pore size distribution of K-0-0 and K-10-500. Both isotherms are Type I according to the BDDT (Brunauer-Deming-Deming-Teller) classification, which elucidates the domination of micropores in the pore structure. The K-10-500 has rather broader pore size distribution than K-O-O, especially below 28 Å, than below 22 Å of K-0-0. This implies that the micropore entrances were blocked with the newly developed nitrogen functional groups produced from propellant waste impregnation and heat-treatment.

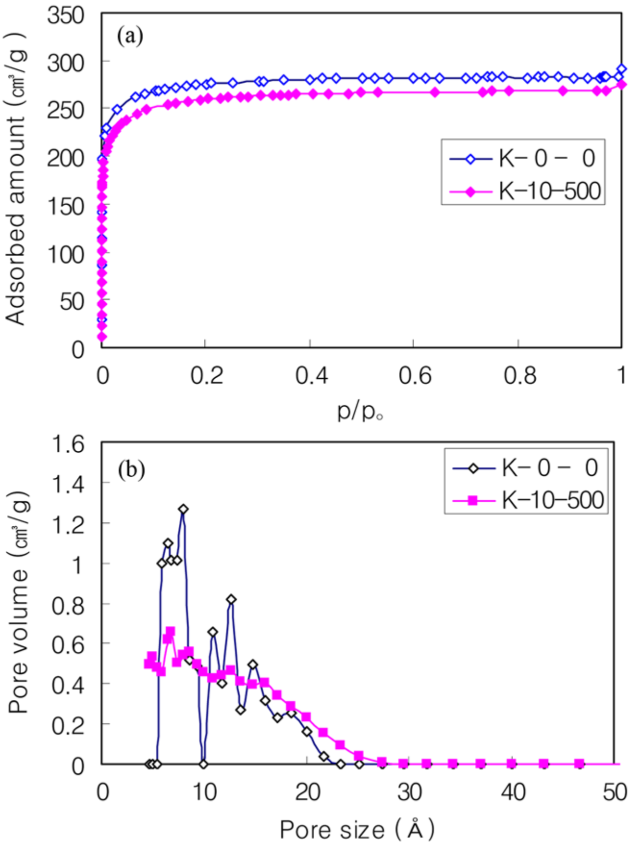


Fig. 1. Adsorption isotherms (a) and pore size distributions (b) of K-0-0 (the as-received) and K-10-500.

2. Thermogravimetric Analysis

Fig. 2 shows TGA curves of the as-received (K-0-0), the 10 wt% propellant waste impregnated (K-10-0), and the heat-treated (K-10-500) ACFs in nitrogen gas.

The weight losses of K-0-0 and K-10-500 were started above 500 °C. On the other hand, the weight loss of K-10-0 was started from 110 °C and rapidly progressed at 190 °C due to the combustion of propellants waste, which was coincided with the ignition point of propellant. It was confirmed that the thermal stability of propellant waste impregnated and heat treated ACF is rather unchangable up to 500 °C.

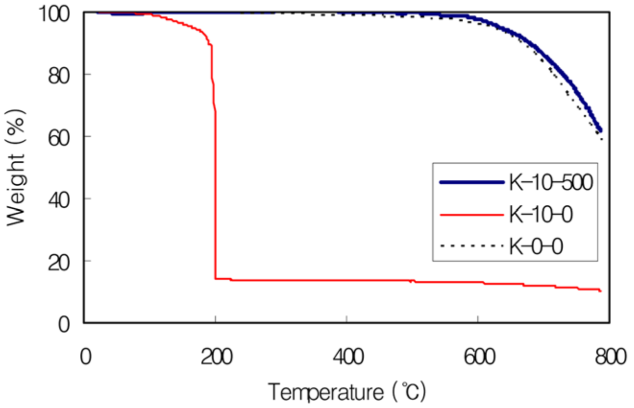


Fig. 2. TGA curve of the as-received and propellant treated ACFs in N$_2$.

Table 1. Structural characteristics of ACFs

ACF	S_{BET} (m^2/g)	V_{Total} (cm^3/g)	$V_{Micropore}$ (cm^3/g)	Average pore size (Å)
K-0-0	927	0.439	0.437	16.9
K-1-500	924	0.436	0.434	17.3
K-5-500	920	0.433	0.430	18.1
K-10-500	910	0.420	0.405	19.9

3. Elemental Analysis

Elemental analysis of ACFs is given in Table 2. Compared with the as-received ACF (K-0-0), the carbon contents of propellants waste modified ACFs decreased with the increase of propellant concentration in solution. Whereas, the content of hetero-atoms such as nitrogen or oxygen was significantly increased, especially the

Table 2. Elemental analysis of the as-received and propellant waste modified ACFs

Samples	Elemental composition (%)			
	C	N	O	H
K-0-0	87.35	0.56	12.41	0.61
K-1-500	86.78	0.62	12.07	0.58
K-5-500	84.20	2.44	13.12	0.89
K-10-500	83.31	3.08	13.68	0.93

Table 3. Superficial composition of ACFs determined by XPS

Samples	Superficial composition (%)		
	C	N	O
K-0-0	87.15	0.58	10.87
K-1-500	84.77	2.73	12.50
K-5-500	80.24	5.52	14.23
K-10-500	78.36	7.40	15.24

nitrogen content increased five times after propellant waste heat-treatment at 500 ºC. These results indicate that nitrogen and oxygen atoms in propellant waste were transferred to the ACF surface through the heat-treatment process. This was also observed from the previous research [17].

The nature of surface functionalities fixed on the surface of ACFs was studied by XPS, which revealed the composition of the most external surface of the ACFs [15,16,19]. Fig. 3 shows the XPS spectra of the as-received and the propellant waste modified ACFs. The major peaks in the spectra were due to the C1s and O1s photoelectrons. The N1s peak of the as-received ACF around 400 eV was very small, while that of propellant waste modified ACFs increased with the increase of propellant waste concentration from 1 to 10 wt%. This means nitrogen groups were introduced on the ACF surface by propellant waste impregnation and heat-treatment and these nitrogen groups might be interacting with the surface carbon to form new surface functional groups, which has resulted in the increase of carbon surface refractoriness [18].

Table 3 shows the superficial composition of ACFs. Atomic ratios were calculated from the XPS spectra after correcting the relative peak areas by sensitivity factors according to the transmission characteristics of the physical electronics SCA [18]. The graphitic carbon content in the as-recieved ACF (K-0-0) hit a peak, while that of nitrogen content shows the lowest value. When propellant waste was impregnated, the nitrogen content gradually increased compared with the as-received ACF. Oxygen content also increased from 10.87 to 15.24% with heat treatment of 10 wt% propellant waste impregnation. This result indicates that the surface functionality of ACF was changed through propellant waste heat-treatment. Nitrogen and oxygen-containing radicals produced during the propellant heat-treatment were easily combined with the surface carbons, resulting in the increase of the nitrogen and oxygen content as expected [17].

4. XPS Study

High-resolution spectra of N1s as shown in Fig. 4 were acquired over 390-405 eV with a step size of 50 meV in order to confirm the nitrogen functional groups. It was convincing that the peak intensities of nitrogen increased to 5,380 cps in proportion to the propellant waste concentration.

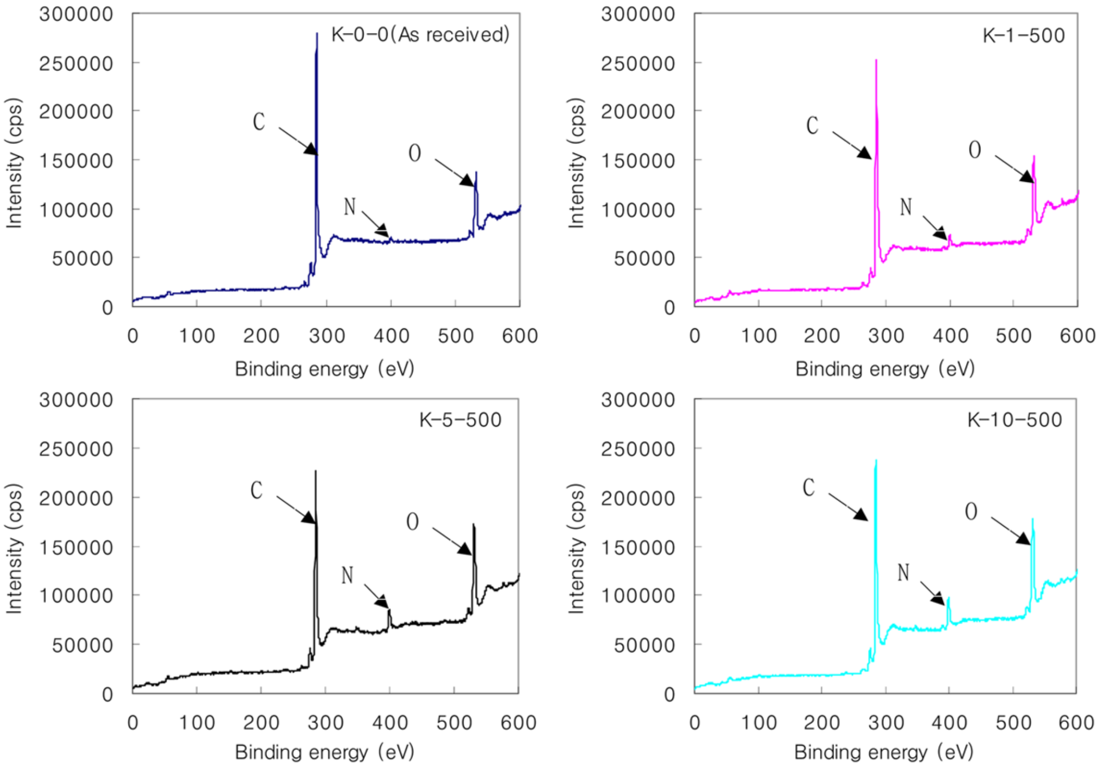


Fig. 3. XPS spectra of the as-received and propellant waste modified ACFs.

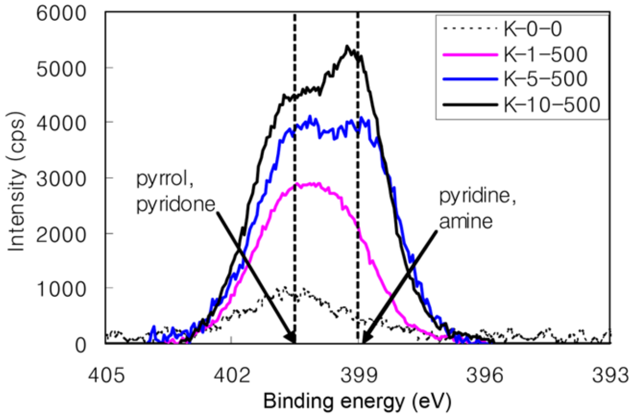


Fig. 4. XPS high resolution N1s spectra of samples.

Fig. 5 shows functional forms and electron binding energy of nitrogen in carbonaceous materials [15,19]. According to the spectra, the major peaks of K-1-500 were confirmed as pyridone or pyrrole (400.5±0.2 eV). The curve configurations of K-5-500 and K-10-500 consisted of two peaks: one is pyridone like species as like that of K-1-500; the other presents pyridine (398.5±0.2 eV).

5. SEM Study

Fig. 6 shows the SEM images of ACF before and after propellant waste heat-treatment. The surface of propellant-impregnated ACF is covered with propellant waste. When propellant-impregnated ACF was heat treated at 500 °C, the surface of K-5-500 looked smooth like as-received ACF (K-0-0). This means the propellant waste was completely oxidized, and developed nitrogen functional groups on the surface of ACF at 500 °C. Compared the SEM images before and after heat-treatment of propellant waste, the ACFs surface was not destroyed after heat-treatment of propellant. This result was very similar to the oxidization of nitrocellulose impregnated ACF [17]. In consideration of pore structure, the newly developed nitrogen groups might be combined with carbon atoms at the entrance of micropores.

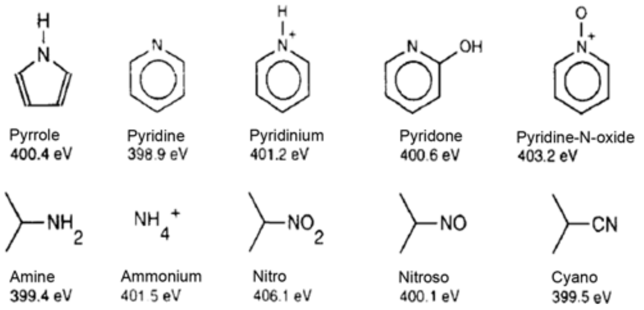
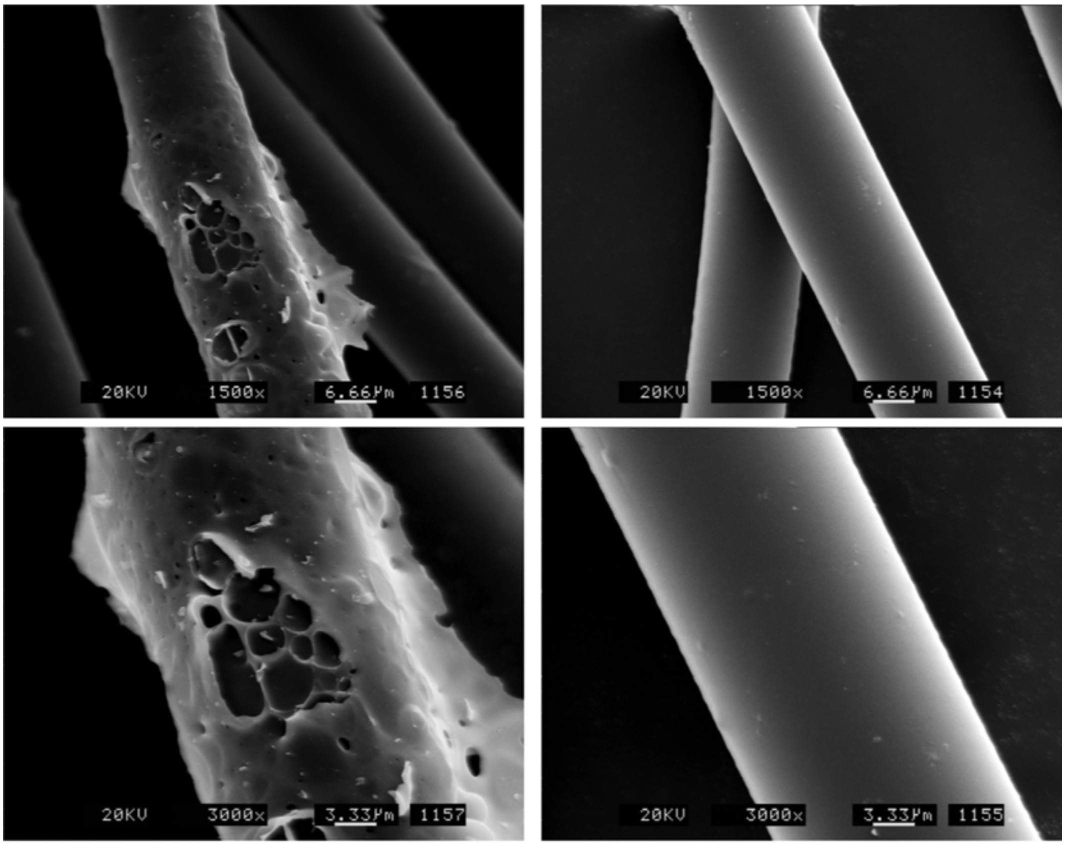


Fig. 5. Nitrogen functional forms in carbonaceous materials, with their N1s electron binding energy [19].

6. NO Removal

Fig. 7 shows the breakthrough profiles of NO and NOx in dry



[Before heat-treatment] [After heat-treatment]

Fig. 6. SEM images before and after heat-treatment of propellant waste.

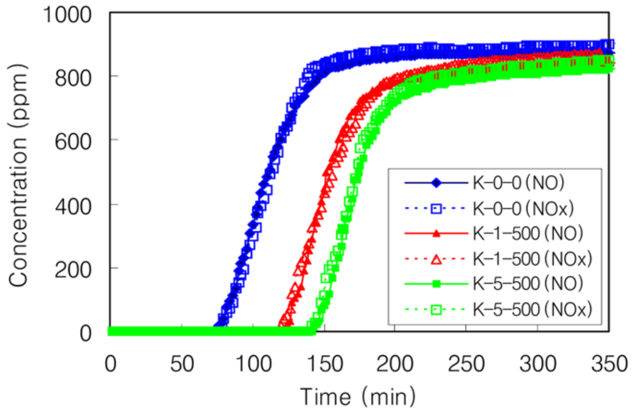


Fig. 7. Breakthrough profiles of NO, NOx on ACF packed bed.

air effused from an ACF packed bed. Complete NO removal was continued by the as-received ACF for 75 min. Then NO and NOx started to effuse from the outlet and the concentration increased rapidly showing the narrow mass transfer zone. This NO removal on the as-received ACF indicates the physical adsorption in micropores. On the other hand, the complete NO removal of propellant waste modified ACFs was extended to 125 minutes and 143 minutes, respectively, depending on the concentration of propellant impregnation. The break point time of the K-5-500 was more than twice of K-0-0. The adsorption capacity was surely extended by the surface functional groups. This extension of NO removal indicates the addition of chemical adsorption to physical adsorption of ACF, which has been confirmed by many other researchers [6-10].

As shown in Fig. 5. the nitrogen functional groups are amine-like species and have basicity, especially the pyridine groups show relatively strong basicity, and have strong affinity to acidic molecules [6,20]. The amine-like species on ACF surface is known to increase the reaction rate between carbon and NOx [6,7]. Reaction of NO with urea supported activated carbons was presented through the following steps [7,21], which might be applied to the amine-like species developed ACFs. The difference between urea and pyridine or pyrrole, etc., is that amine is bonded to aromatic groups.

$$NO+1/2\,O_2 \rightarrow NO_2 \qquad (1)$$

$$NO_2+NO+(NH_2)_2CO \rightarrow 2N_2+CO_2+H_2O \qquad (2)$$

ACF with higher surface nitrogen content tended to have higher NO removal capacity on the basis of direct interaction of nitrogen function group such as pyridine, pyrrole, and amine. Therefore, the porous carbons developed nitrogen functional groups on the surface which can extend the removal capacity of NO and NOx in addition to the physical removal capacity, and the propellant waste can be used as a useful surface modifier of carbon adsorbents.

CONCLUSIONS

Nitrogen functional groups can be introduced on the surface of activated carbon fiber by simple and controllable impregnation and heat-treatment of propellant waste. The diameter of micropores can be slightly broadened due to the blocking of newly introduced functional groups at the entrance of micropores. However, there is no morphological damage on the surface of porous carbon by heat-treatment of propellant waste. The newly introduced nitrogen functional groups are pyridine, pyridone, and pyrrol. The introduced nitrogen functional groups on ACF can chemically enhance the NO removal capacity in addition to physical removal at ambient temperature. The propellant waste can be used as a useful surface modifier of carbon adsorbents instead of simple disposal.

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