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Effect of Temperature on the Adsorption and Desorption Characteristics of Methyl Iodide over TEDA-Impregnated Activated Carbon

Geun-Il Park♠, In-Tae Kim, Jae Kwang Lee*, Seung Kon Ryu* and Joo Hyung Kim

Korea Atomic Energy Research Institute, Daejon 305-353, Korea
*Dept. of Chemical Engineering, Chungnam National University, Daejon 305-764, Korea
♠e-mail: *ngipark@kaeri.re.kr*
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Abstract

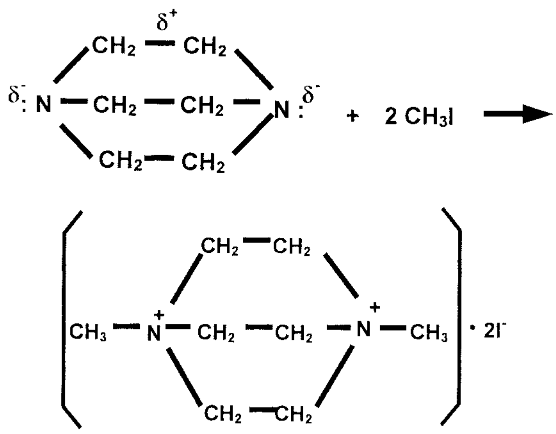
Adsorption and desorption characteristics of methyl iodide at high temperature conditions up to 250°C by TEDA-impregnated activated carbon, which is used for radioiodine retention in nuclear facility, was experimentally evaluated. In the range of temperature from 30°C to 250°C, the adsorption capacity of base activated carbon decreased sharply with increasing temperature but that of TEDA-impregnated activated carbon showed higher value even at high temperature ranges. Especially, the desorption amount of methyl iodide on TEDA-impregnated carbon represented lower value than that on unimpregnated carbon. The breakthrough curves of methyl iodide in the fixed bed packed with base carbon and TEDA-impregnated activated carbon at high temperature were compared. TEDA-impregnated activated carbon would be applicable to adsorption process up to 150°C for the removal of radioiodine in a nuclear facility.

Keywords : *TEDA-AC, High temperature, Methyl iodide, Adsorption, Desorption*

1. Introduction

During the operation of nuclear power plants or nuclear facility, various radioactive gaseous wastes are generated. Because radioiodine among these gaseous wastes has radiological harm on the human body and environment, it is significantly considered that this gas must be removed below restriction of release even in the case of normal operating and accident conditions. Therefore, numerous studies for the removal of radioiodine from the off-gas stream of nuclear facilities have been performed with formation processes and chemical structure [1-6]. Radioiodine generated from nuclear power plants are partially converted radioactive organic iodide, such as methyl iodide, by react with organic matter in process line. TEDA (TriEthyleneDiAmine) or KI-impregnated activated carbons are, in general, used to effectively remove the radioiodine under an accident of high humidity condition.

TEDA, 1,4-Diazabicyclo(2.2.2)octane(DABCO), has a molecular formula of $C_6H_{12}N_2$ with a molecular efficiency by forming charge transfer complexes with organic iodies. The impregnated TEDA on activated carbon is converted quaternary ammonium salts by react with organic iodies as following [7].



There has been some concern regarding the use of TEDA-impregnated activated carbon as an adsorbent for radioiodine removal, because of the low ignition point of TEDA and the possible release of TEDA from the charcoal in continuously flowing air streams. The ignition point of TEDA-impregnated carbon has been reported to be about 190°C [7]. It has been reported that the release of up to 1.2 μg TEDA/(g carbon, min) is observed from various TEDA at 90°C and a flow rate of 4.7 cm/s [7, 8]. Therefore, the TEDA-impregnated activated carbon cannot use in high temperature systems, such as the sintering step in DUPIC (Direct Use of Spent PWR Fuel In CANDU Reactor) process, due to the rapid drop of the removal efficiency and the ignition possibility of activated carbon at this condition. Extensive studies in our laboratory were focused to perform the domestic self-development of silver ion-exchanged inorganic solid adsorbent for the removal of radioiodine at high temperature. These works include the adsorption characteristics and the overall evaluation of removal efficiency of radiodine in fixed bed packed with silver ion-exchanged zeolite [9, 10].

Silver zeolite is an expensive adsorbent due to the cost of silver reagent, compared to TEDA impregnated activated carbon whose application to high temperature has some limitations. It is obvious that high temperature can be expected during design basis loss-of-coolant accident (LOCA), which can be regarded as conservatively representing the temperature in pressurized water reactor (PWR). Therefore, investigation on the retention of elemental radioiodine (^{131}I) by various activated carbons at high temperature has extensively been performed so far [11-13]. But only a few results on the adsorption of methyl iodide at high temperature condition have also been presented.

In this study, the adsorption and desorption characteristics of methyl iodide on the TEDA-impregnated activated carbon in fixed bed at high temperature up to 250^{o}C were evaluated with respect to the variation of temperature. Based on the removal efficiency and desorption amount of methyl iodide obtained from the experimental results, the temperature limit of TEDA impregnated activated carbon in application to high temperature ranges is also suggested.

2. Experiment

2.1. Materials

Base activated carbon (AC) and TEDA-impregnated activated carbon (TEDA-AC) were used to examine the adsorption capacity of methyl iodide at various temperature. Activated carbon made from coconut shells, supplied by Samchulri Carbon Co., Korea, with a particle size 8~16 mesh was used.

TEDA-impregnated activated carbons with 6.5 wt% of TEDA were made by impregnating with chemical reagents on the base carbon according to the method presented in a patent [14]. Virgin activated carbon was dried at 110^{o}C for 24 hours to remove moisture. The impregnation time was about 30 minutes, and the ratio of TEDA solution volume to weight of AC was 1.2 ml/g. After impregnation, TEDA-AC was dried at 70~80^{o}C for 16 hrs. The amount of impregnant on TEDA-AC was obtained by the extraction of TEDA with acetonitrile solution and then the analysis of solution concentration using UV-Spectrophotometer. The physical property of two carbons with the aid of the BET-N_2 (Micromeritics, ASAP 2400) analysis was obtained, as listed in Table 1.

The physical properties of TEDA-AC were similar to these of the AC, except for a slight decrease on pore volume and surface area.

Table 1. Physical characteristics of Adsorbents

Characteristic	Base AC	TEDA-AC (6.5 wt%)
Mean Pore Diameter (Å)	12	13.2
Pore Volume (cm^3/g)	0.767	0.658
Micro Pore Volume (cm^3/g)	0.592	0.523
Surface area (m^2/g)	1,483	1,275

2.2. Experimental Apparatus and Methods

A schematic diagram of experimental apparatus is shown in Fig. 1. All parts of the system, such as adsorption column and gas flow lines, were made of pyrex glass to prevent the elemental iodine plate-out and trapping. Gaseous methyl iodide is produced from an evaporation of methyl iodide solution. The gas-phase concentration is adjusted by controlling the solution temperature and the nitrogen flow rate to methyl iodide generators. Dry air was used as a carrier gas at 4 *l*/min, a superficial velocity of 0.18 m/sec.

The temperature inside the adsorbent was controlled up to 400^{o}C by heating the column in an electric furnace. A constant amount of the adsorbents is packed in a column with dimensions of 0.022 m I.D. and 0.6 m length, and these adsorbents were thermally equilibrated with the gaseous-phase. The effluent concentration of methyl iodide from the column was analyzed by the gas chromatography with a pulse discharged detector (PDD) and GS-Q capillary column at an oven temperature of 140^{o}C as shown in Table 2. Both the breakthrough curve of methyl iodide adsorption and the weight change of the adsorbent were used to obtain the adsorption amount of the adsorbate. Also, desorption experiment after adsorption of methyl iodide was conducted by controlling the column temperature.

Adsorbed amount of methyl iodide by chemical reaction with only TEDA is calculated by following equation, based on the experimental data obtained from fixed bed adsorption. One mol of TEDA can be stoichiomatically adsorbed the two mole of methyl iodide.

Adsorbed amount of methyl iodide by TEDA on TEDA-AC =

$$\frac{\text{(Total adsorption amount by TEDA AC}-\text{Total adsorption amount by AC, mol/g)}}{\text{TEDA amount on TEDA}-\text{AC(mol/g)}}\times 100$$

3. Results and Discussion

3.1. Removal Efficiency of Methyl Iodide

In order to analyze the adsorption and desorption characteristics of methyl iodide by TEDA-AC at high temperature range, adsorption behavior of methyl iodide on AC and TEDA-AC at room temperature was evaluated at first. These works were performed in a thin bed with the depth of 3 cm.

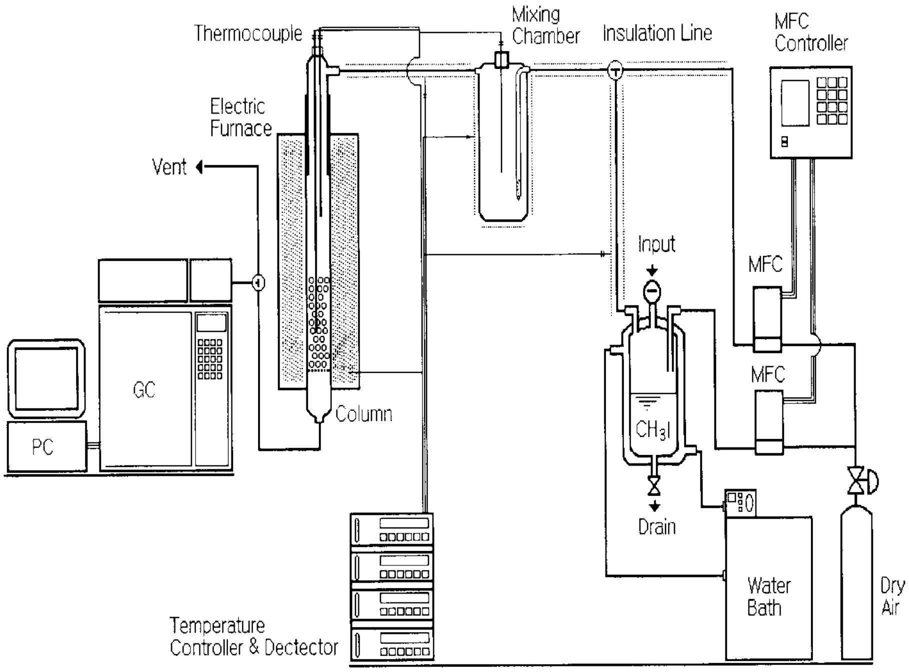


Fig. 1. Flow diagram of the experimental apparatus for methyl iodide.

Table 2. Experimental and gas chromatography conditions

Experimental parameters	Conditions	Unit
Process flow	4.0	*l*/min
Superficial velocity	0.18	m/sec
Bed depth	10	cm
Input concentration	4×10^{-6}~6×10^{-5}	mol/L
Gas(CH_3I) generator temperature	30	°C
Bed temperature	30~250	°C
Relative humidity	Dry	%
GC analysis conditions		
– Capillary column	GS-Q	
– Detector	PDD	Pulse Discharged Detector
– Carrier gas(He) flow rate	6	ml/min
– Oven temperature	140	°C
– Detector temperature	160	°C
– Auto sampler volume	1.0	ml

Fig. 2 and 3 represent the breakthrough curves of methyl iodide adsorption on AC and 6.5 wt% TEDA-AC as a function of input concentration at 30°C. As the input concentration is increased, it is normal that breakthrough time becomes short. At the same input concentration in thin bed of 3 cm, adsorption capacity of AC is slightly higher than that of TEDA-AC due to the decrease of surface area as shown in Table 1. This means that adsorption capacity at room temperature depends on both the physical adsorption and chemical adsorption. However, TEDA-AC is more useful to retain the adsorbed methyl iodide, because the retention of methyl iodide by TEDA is due to chemical reaction. This result will be discussed in the next section. In general, the amount of TEDA on carbon filter installed in nuclear facility ranges from 2 wt% to 5 wt% [12]. The influence of TEDA amount on adsorption of methyl iodide at 30°C was evaluated. Fig. 4 shows that increase of TEDA amount made a short breakthrough time. Nevertheless, it is thought that the effect of TEDA inpregnation on the adsorption capacity at room temperature is minimal.

During a postulated nuclear reactor accident, the radioiodine buildup on carbon filters would be high. The highly radioactive iodine would not only provide the intensive radiation field within the carbon filter, but also it would signifi-

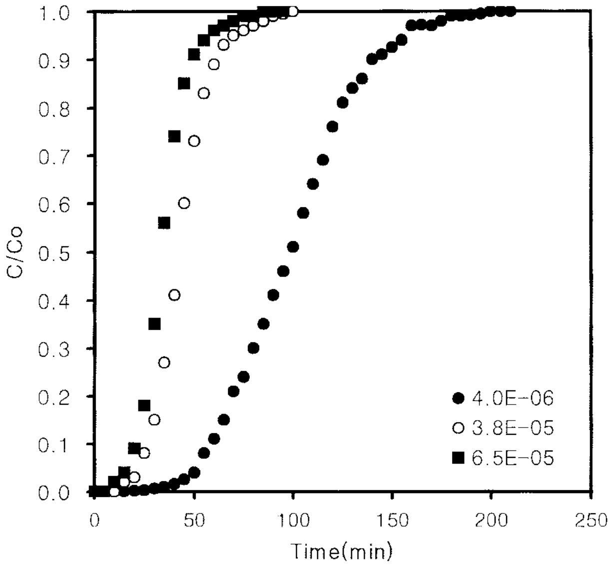


Fig. 2. Breakthrough curves of methyl iodide adsorption on AC with input concentrations (Bed Depth=3 cm, Temp.=30°C).

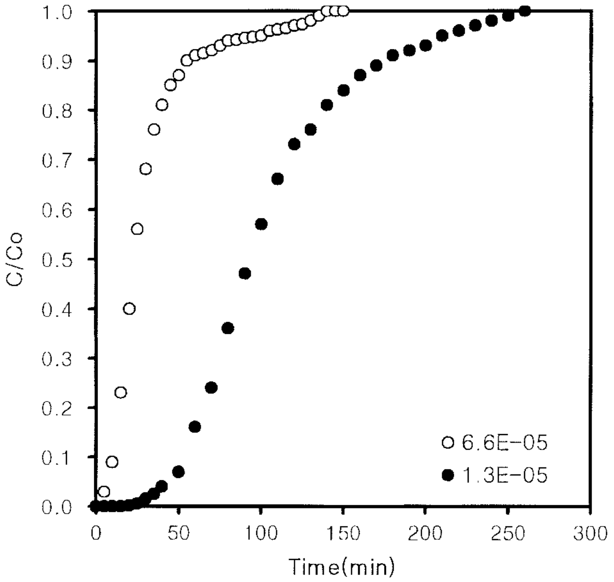


Fig. 3. Breakthrough curves of methyl iodide adsorption on 6.5 wt% TEDA-AC with input concentrations (Bed Depth=3 cm, Temp.=30°C).

cantly increase the carbon temperature because of decay heat. Therefore, breakthrough curves of methyl iodide adsorption on AC and 6.5 wt% TEDA-AC at high temperature ranges up to 150 °C were obtained in thin bed of 3 cm, as shown in Fig. 5 and 6, respectively. Input concentration was about 5×10^{-5} mol/*l* in all experiments. Overall breakthrough behavior was the same; as the temperature increases, the adsorption capacity decreases. Especially, above 75°C breakthrough time sharply decreased. This result would be

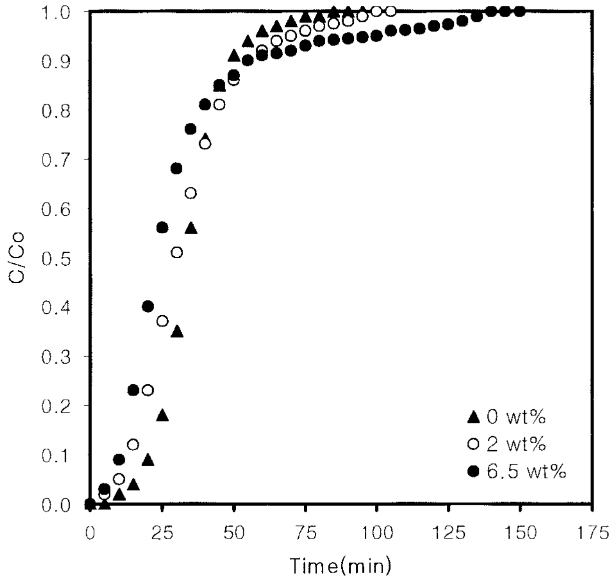


Fig. 4. Breakthrough curves of methyl iodide adsorpt6ion on various TEDA-AC at input concentration of 6.6×10^{-5} mol/l (Bed Depth=3 cm, Temp.=30°C).

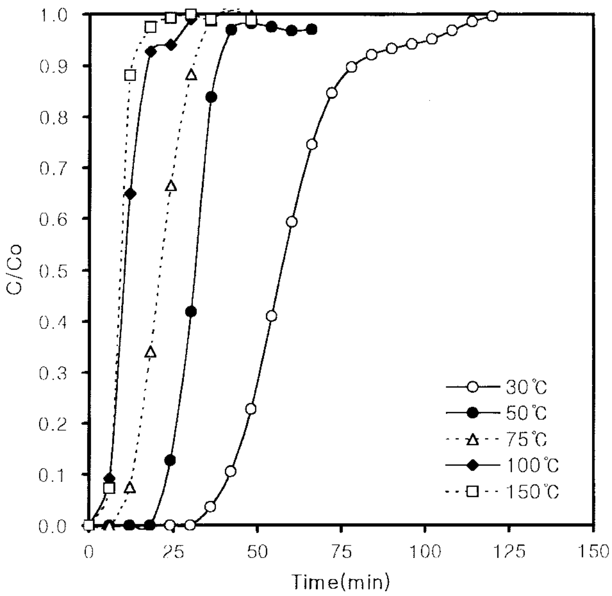


Fig. 5. Breakthrough curves of methyl iodide adsorption on AC with variation of adsorption temperature (Bed Depth=3 cm, Co=5×10^{-5} mol/l).

caused by the decrease of physisorption amount, the release of TEDA and the increase of desorption rate of adsorbed methyl iodide with increasing temperature.

The carbon filter used in a nuclear facility has general dimension, that is, bed depth is 25 cm and face velocity of air stream to carbon filter is about 25~50 cm/sec [12]. Fig. 7 represents the breakthrough curves of methyl iodide adsorption on AC and 6.5 wt% TEDA-AC at temperature of 100°C

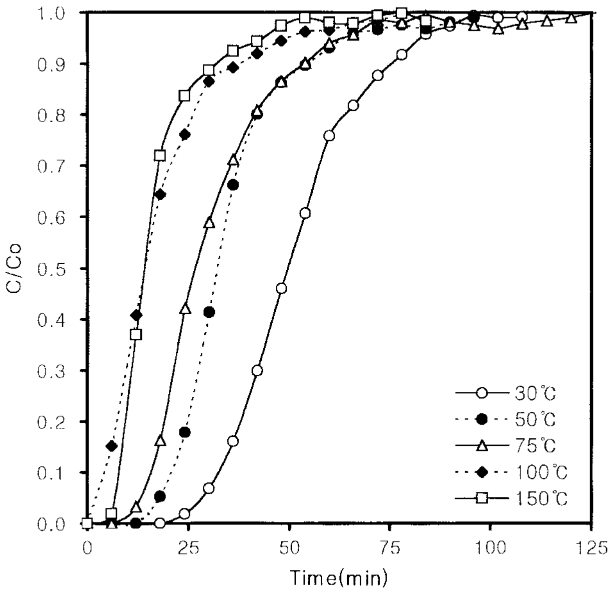


Fig. 6. Breakthrough curves of methyl iodide adsorption on 6.5 wt% TEDA-AC with variation of adsorption temperature (Bed Depth=3 cm, Co=5×10^{-5} mol/l).

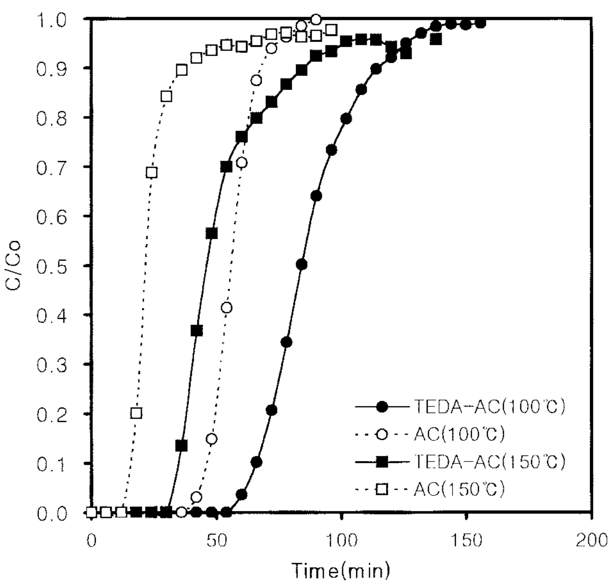


Fig. 7. Breakthrough curves of methyl iodide with temperature in deep bed packed with AC and 6.5 wt% TEDA-AC. (Bed Depth=10 cm, Co=5×10^{-5} mol/l).

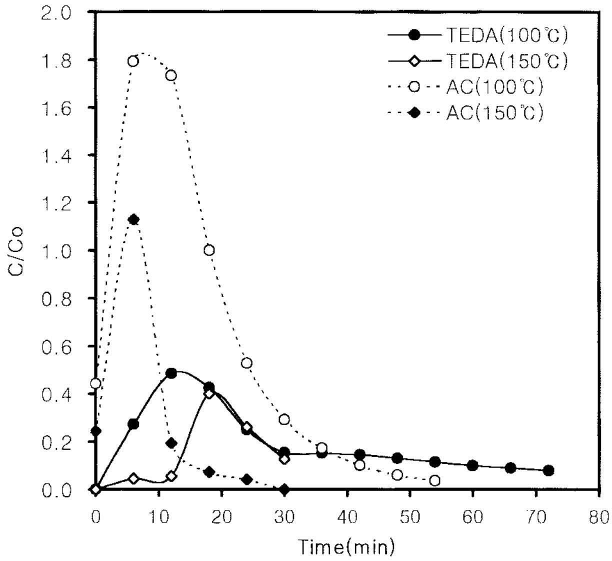


Fig. 8. Desorption curves of methyl iodide with temperature in deep bed packed with AC and 6.5 wt% TEDA-AC. (Bed Depth=10 cm, Dry Air).

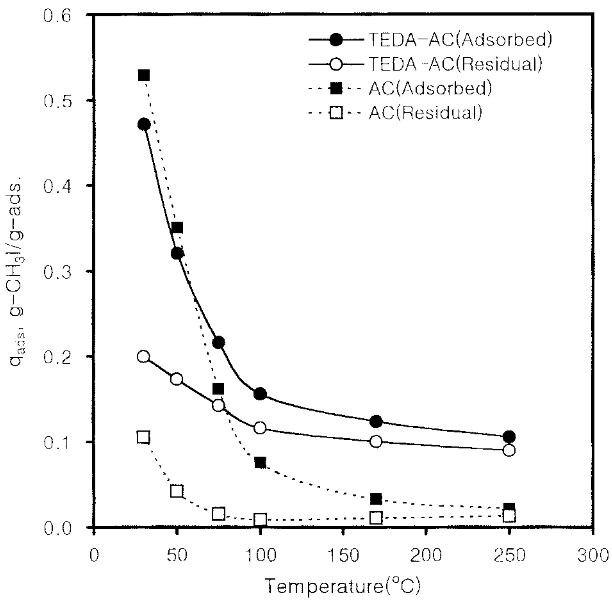


Fig. 9. Adsorption amount and residual amount after desorption with temperature on AC and 6.5 wt% TEDA-AC. (Bed Depth =3 cm, Co=5×10^{-5} mol/l).

and 150°C under the same input concentration in a deep bed of 10 cm. Adsorption capacity of TEDA-AC at 100°C and 150°C was higher than that of AC, and the increased bed temperature reduced the adsorption capacity of TEDA-AC for methyl iodide removal. A little difference on adsorption capacity at thin bed of 3 cm in the range of 100°C to 150°C was observed, as shown in Fig. 6. This is likely due to an increase of temperature inside bed by adsorption heat generated from the chemical reaction. Fig. 8 shows the concentration variation with time during desorption test for TEDA-AC and AC adsorbed methyl iodide (refer to Fig. 7). TEDA-AC had a low desorption amount at high temperature, as compared with that of AC.

3.2. Quantitative analysis of sorption amount

The adsorbed amount and the residual amount of methyl

Table 3. Adsorption amount and residual amount after desorption of methyl iodide (unit: g/g-adsorbent)

Temp. (°C)	AC		TEDA-AC	
	Adsorption	Residual	Adsorption	Residual
30	0.529	0.105	0.470	0.199
50	0.350	0.041	0.320	0.172
75	0.161	0.015	0.215	0.141
100	0.074	0.008	0.155	0.115
170	0.032	0.010	0.123	0.100
250	0.021	0.011	0.105	0.089

iodide after desorption test on each of the adsorbents in the temperature range of 30°C to 250°C are shown in Fig. 9. Quantitative data are listed in Table 3.

As mentioned before, the adsorption capacities of TEDA-AC and AC decrease with increasing temperature. TEDA-AC had a higher adsorption capacity than AC beyond 70°C, and a little difference between the adsorbed amount and the residual amount was observed. These results suggest that the adsorption capacity of AC results from almost physical adsorption, but TEDA is effective in strong fixation of methyl iodide at higher temperature by chemical reaction. Based on the previous equation, the degree of contribution on the adsorbed amount of methyl iodide by only TEDA was calculated at various temperatures. These results are 25.4% at 75°C, 51.9% at 100°C, and 73.3% at 150°C, respectively. Therefore, it would be confirmed that the impregnated TEDA contributes to the removal of methyl iodide at high temperature ranges.

Although impregnated TEDA on TEDA-AC can be released at high temperature, TEDA-methyl iodide complex due to chemical reaction was very stable. In the previous study [6], a pure TEDA begin to vaporize at 174°C, a TEDA-methyl iodide complex begin at 270°C and a TEDA-methyl iodide on TEDA-AC begin to decompose at 200°C. Based on these results, TEDA-AC would be used to remove radioiodine below 150°C. However, it is necessary to confirm the possibility of ignition by adsorption heat.

4. Conclusion

TEDA-impregnated activated carbon is generally used to remove radioiodine generated from normal operating conditions or accident conditions in a nuclear power plant. Therefore, adsorption and desorption characteristics of methyl iodide at high temperature conditions up to 250°C by TEDA-impregnated activated carbon, which represents the performance test at accident condition, was experimentally evaluated. In the range of temperature from 30°C to 250°C, the adsorption capacity of base activated carbon sharply decreased with increasing temperature but that of TEDA-impregnated activated carbon showed higher value even at high temperature ranges. It was obvious that TEDA-AC had higher adsorption capacity than AC beyond 70°C, and a little difference between the adsorbed amount and the residual amount after desorption was observed. These results suggest that the adsorption capacity of AC is largely due to physical adsorption, but TEDA is effective in strong fixation of methyl iodide at higher temperature by chemical reaction. Based on these results, TEDA-impregnated activated carbon would be applicable to temperature up to 150°C for the removal of radioiodine in nuclear facility. However, the possibility of ignition due to adsorption heat and decay heat in deep bed should be confirmed.

Acknowledgment

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