*Korean J. Chem. Eng.*, **30**(4), 891-897 (2013)
DOI: 10.1007/s11814-012-0179-9

# Evaluation of physical properties and adsorption capacity of regenerated granular activated carbons (GACs)

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(*Received 7 June 2012 • accepted 17 October 2012*)

**Abstract**−The objectives of this study were to evaluate the variation in physical properties and investigate the adsorption capacity after regeneration of granular activated carbon (GAC). A correlation analysis was conducted to examine the relationship between the iodide number and loss rate. The experimental results showed that the loss rate of regenerated carbon should be related to the usage time of GAC. Physical properties including the effective size and uniformity coefficient were similar to those of virgin GAC. This result indicates that the function of GAC as an adsorption medium may be recovered completely. Although the iodine number and specific surface area of the regenerated GAC were smaller than those of virgin GAC, the cumulative pore volume of the former was larger. The removal efficiency of organic matter from the regenerated GAC column was equal to or slightly higher than that from the virgin GAC column. Consequently, regeneration may increase the number of mesopores which are responsible for the removal of organic matter.

Key words: Granular Activated Carbon (GAC), Regeneration, Physical Properties, Adsorption Capacity, Iodide Number

## INTRODUCTION

At present, the granular activated carbon (GAC) adsorption process is widely used to remove organic micro-pollutants at water treatment plants (WTPs). Further, in order to control the taste and odor matter of the source water, the GAC process is generally applied or added to conventional WTPs as the best available technology (BAT). Accordingly, application instances can be expected to continuously and substantially increase to meet consumer requirements and criteria for drinking water standards.

However, GAC has limited adsorption capacity and is a relatively costly material. Generally, the adsorption capacity of used GAC can be recovered by heat regeneration, and the regenerated GAC can be reused as adsorption media similar to virgin GAC. The economical feasibility or efficiency of GAC strongly depends on the activated carbon usage rate (CUR), which is the mass of activated carbon used per unit volume of water treated. Therefore, regeneration of the used GAC is thought to be more economically feasible than replacement with virgin GAC.

$$\text{Carbon usage rate (CUR)} = \frac{\text{mass of GAC in column}}{\text{volumn treated}} \qquad (1)$$

A previous study showed that the cost of regenerated GAC is 40-60% less than that of virgin GAC [1]. Considering a preliminary estimation in Korea, the cost of regenerated GAC is 30-50% less.

In Korea, the government and local facilities have recently invested in the construction and operation of advanced water treatments such as ozone and GAC processes to control taste and odor matter in drinking water. Thus, there is an urgent need to determine the optimal time for replacement with virgin GAC or regeneration of the used GAC. Moreover, since a sharp increase in the price of virgin GAC is expected, plans for virgin GAC replacement at every WTP are recognized as economically in feasible.

A few previous studies investigated the feasibility of regenerated GAC with regard to whether its quality and adsorption capacity are appropriate for reuse from the viewpoint of economic efficiency. The objective of this study was to evaluate the variations in physical properties of regenerated GAC that had been used as adsorption media in Korean domestic pilot plants for a long time. Further, by comparing their adsorption capacity with that of virgin GAC, the feasibility of regeneration was investigated.

## MATERIAL AND METHODS

### 1. Used GAC Selection

The used GACs were selected to evaluate removal efficiency of organic matter and adsorption capacity after regeneration; five samples were used in total (refer to Table 1). Two samples (GAC-5Y, GAC-5Y-EBCT 7) had been used at the SJ_WTP pilot plant for five years, one sample (F/A-3Y) had been used at the BW_WTP pilot plant for three years, one sample (F/A-BW-1.1Y) had been used at the BW_actual WTP for 1.1 years, and one sample (F/A-BS-2.6Y) had been used at the BS_actual WTP for 2.6 years. Tables 1 and 2 show the characteristics of the used GACs and the specifications of their virgin states, respectively.

### 2. Regeneration Method

The used GACs were regenerated in a rotary tube furnace consisting of a steam boiler, regeneration furnace, heat exchanger, and blower (Fig. 1); the furnace can regenerate about 2 kg. The operation conditions are as follows: nitrogen gas is injected at 20 L/min, the furnace temperature is raised at 5 °C/min, steam is injected (82 g/

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**Table 1. Characteristics of the used GACs**

| Samples | GAC-5Y | GAC-5Y-EBCT 7 | F/A-3Y | F/A-BW-1.1Y | F/A-BS-2.6Y |
|---|---|---|---|---|---|
| WTP | SJ (pilot scale) | SJ (pilot scale) | BW (pilot scale) | BW (actual plant) | BS (actual plant) |
| Processes | GAC adsorber | Post $O_3$*+GAC adsorber | Pre $O_3$+F/A** | F/A** | F/A** |
| Source water | Han river | Han river | Han river | Han river | Nakdong river |
| Usage time (years) | 5 | 5 | 3 | 1.1 | 2.6 |
| Bed volume (volume treated/ volume of column) | 188,000 | 376,000 | 118,000 | 40,000 | 112,000 |
| Types | Calgon 1240<br>F-400 | Calgon 1240<br>F-400 | Calgon 820<br>F-820 | Calgon 820<br>F-820 | Calgon 820<br>F-820 |
| Particle diameter (mm) | 0.42-1.68 | 0.42-1.68 | 0.84-2.36 | 0.84-2.36 | 0.84-2.36 |
| Empty bed contact time (EBCT) (min) | 14 | 7 | 14 | 14 | 12 |

* $O_3$ means ozonation process

** F/A means GAC filter-adsorber

**Table 2. Specifications of the selected GAC types**

| Parameters | Calgon corp. | |
|---|---|---|
| Product name | F-400 | F-820 |
| Raw material | Coal | Coal |
| Effective size (mm) | 0.55-0.75 | 1.0-1.2(1.2) |
| Mesh size | 12×40<br>≥1.68 mm ≤5%<br>≤0.42 mm ≤4% | 8×20<br>≥2.38 mm ≤5%<br>≤0.84 mm ≤4% |
| Mean particle diameter (mm) | 0.9-1.1 | 1.6 |
| Dry weight (%) | ≤2 | 2.0 |
| Hardness (%) | ≥90 | 95-97 |
| Uniformity coefficient | 1.5-1.9 | 1.5 |
| Density (g/$cm^3$) | 0.45 | 0.50-0.57 |
| Surface area ($m^2$/g) | 1,050-1,250 | 1,027 |
| Iodine number (mg/g) | ≥1,050 | ≥900 |
| Pore volume (cc/g) | 0.85-0.95 | 0.53 |

min) into the furnace at 930 °C for about 30 min, and the regenerated carbon is cooled physically.

### 3. Methods for Analyzing Physical Properties

The iodine number, which represents the mass of the absorbed iodine per unit gram activated carbon (mg/g), can be measured by the KSM 1802 method [2]. To determine iodine number, the iodine solution (0.005 M, 50 mL) should be added to 0.5 g targeted activated carbon and adsorbed forcibly. Unreacted iodine in the mixture reacts with potassium iodide to convert to iodine, whose concentration can be determined by titration with sodium thiosulfate (0.1 M). By using the adsorption-desorption isothermal curve derived from nitrogen ($N_2$, 17-2,000 Å) and argon (Ar, 3.5-1,000 Å), the pore structural characteristics of the selected GACs were analyzed with an ASAP 2020 Sorptometer (Micromeritics Instrument Corp. Norcross, GA, USA). The specific surface area and pore size distribution were calculated from the Brunauer-Emmet-Teller (BET) [3] and Barrett-Joyner-Halenda (BJH) equations [4]. The surface structures of each GAC were investigated by a scanning electron microscope/energy dispersive X-ray spectrometer (SEM/EDS) (JEOLJSM-840A SEM/LINK system AN-10000/85S EDSW-hairpin type gun, X10-X300,000, SEI (4.0 nm), BSI (10.0 nm). 0.2-40 kV).

The concentrations of dissolved organic carbon (DOC) in samples from each column were measured as prescribed by the persulfate-ultraviolet oxidation method of Standard Methods 5310 C [5] using a Dohrman TOC analyzer (Phoenix 8000).

### 4. Methods for Evaluating Adsorption Capacity

A rapid laboratory scale column test was conducted to evaluate the adsorption capacity of the regenerated GACs for organic matter [6,7]. As shown in Fig. 2, the virgin and regenerated GACs (12×40 mesh, average particle diameter: 1.0 mm) were ground by pestle and mortar; both were sieved with a 100×200 mesh to have an average diameter of 0.11 mm for the column test. The GACs were washed repeatedly until the washing water no longer turned black. They were then dried in an 85 °C oven for 24 h. Before the columns were filled with GACs, the dried GACs were submerged inside distilled water in a vacuum for 12 h to remove air bubbles attached to GACs surface. The columns were made of Teflon; the inner diameter was 3.9 mm, and the length was 8.3 cm. All connection pipes were made of stainless steel (SUS 304). The test columns were geometrically scaled down by a factor of 9.44 from the actual GAC absorbers. To minimize head loss for testing, a pre-filter made of glass fiber was set at 3 cm in the inlet of each column. The depths of the GACs were calculated for empty bed contact times (EBCTs) of 7 and 14 min (refer to Fig. 2). Inlet flow rates to the column were fixed to a constant Q=1.34 mL/min during each test. Samples were taken every 6 h to measure the water quality.

## RESULTS AND DISCUSSIONS

### 1. Physical Properties of the Regenerated GACs

Fig. 3 shows the variation in iodine number according to usage time. For reference, the iodine numbers of the virgin GACs F-400 and F-820 (Calgon Corp.) were 1,038 and 1,146 mg/g, respectively. The iodine number of the GAC used for 1.1 years (F/A-BW-1.1Y) and sampled from BW_WTP decreased to 704 mg/g, that of the GAC used for 2.6 years (F/A-BS-2.6Y) from BS_WTP was 487 mg/g, and that of the GAC used for three years (F/A-3Y) from BW_pilot plant was 369 mg/g. In addition, the iodine number of the GAC sample used for five years from SJ_pilot plant decreased to 297 mg/

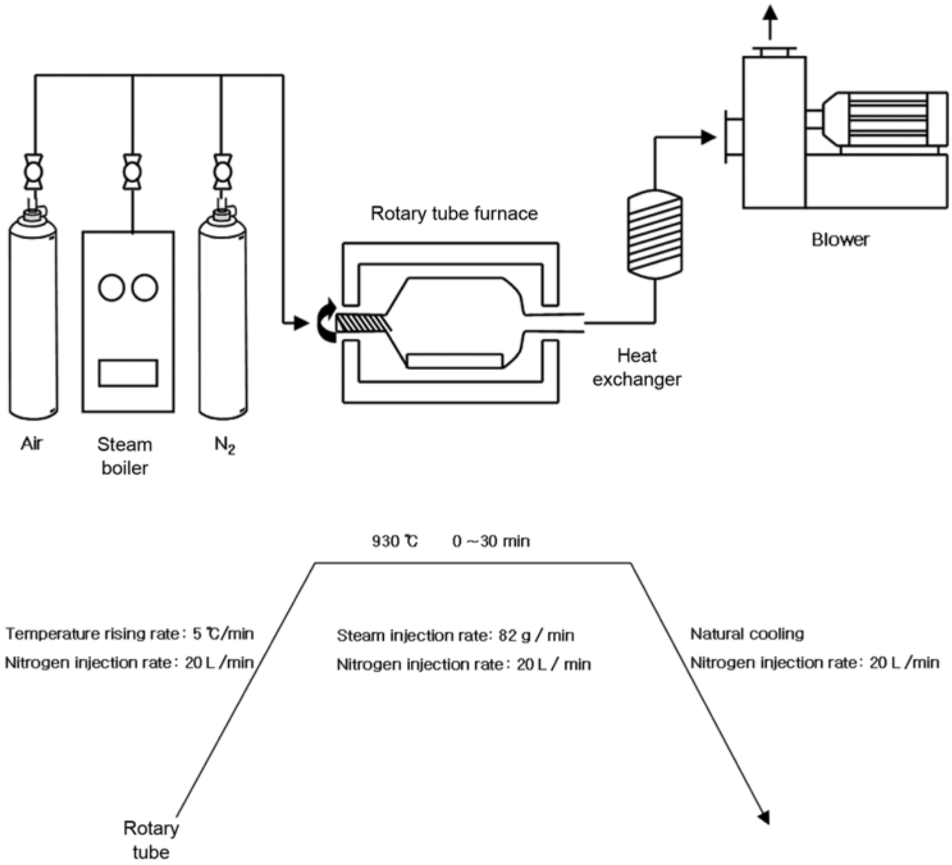


**Fig. 1. Rotary tube furnace and its operating conditions.**

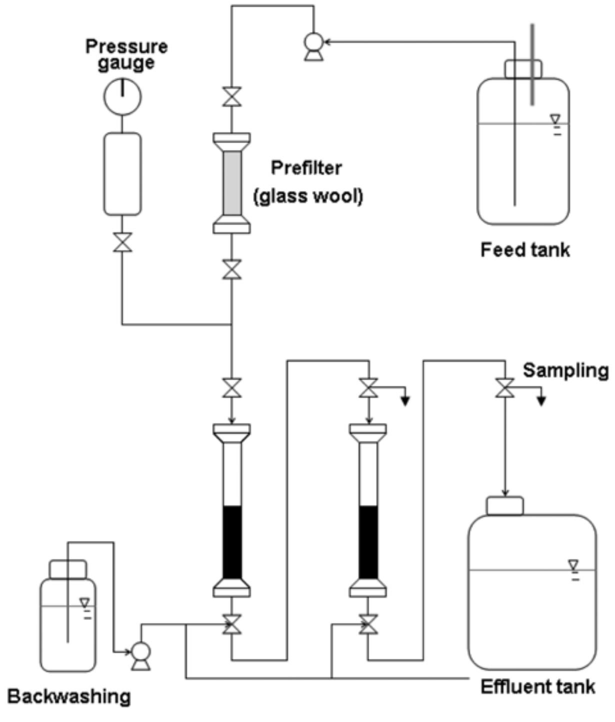


**Fig. 2. Schematic diagram of rapid laboratory scale column test.**

g. These results show that the iodine number decreases sharply from the virgin state for 2-3 years and that the reduction rates slow down as the usage time is prolonged beyond this period. By regressing the iodine number data according to the usage time from Fig. 3, the relationship between the iodine number and usage time was derived as follows in Eq. (2).

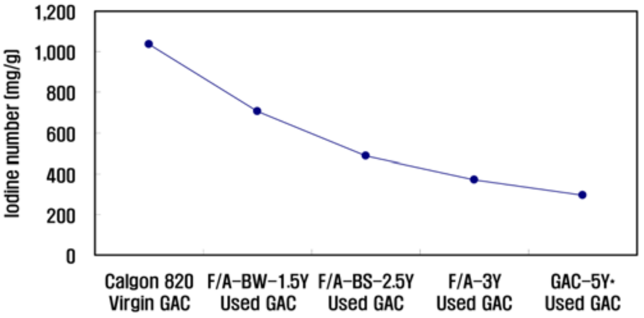
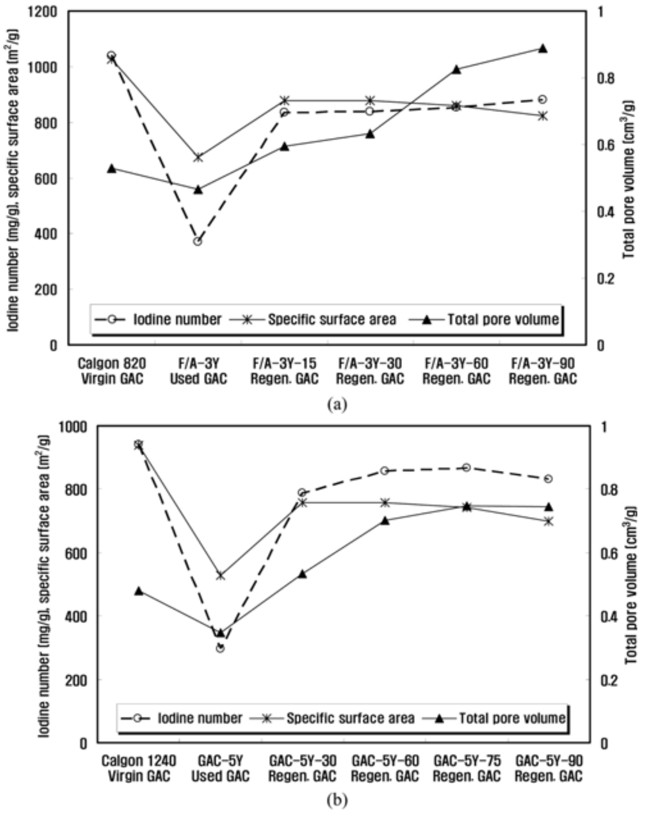


**Fig. 3. Variation in iodine number according to usage time.**

$$Y^2=32.4X^2-308.5X+1028.5, \qquad R^2=0.99 \qquad (2)$$

where is the iodine number (mg/g) and is the usage time (years).

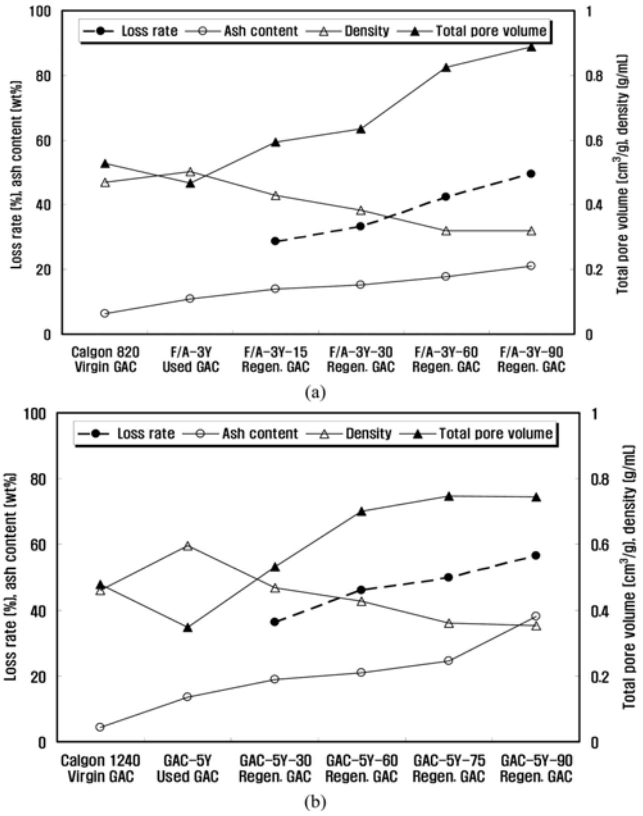
Fig. 4(a) shows the iodine number, specific surface area, and total pore volume of the virgin GACs (Calgon 820), F/A-3Y (GAC used for three years), F/A-3Y-15 (when regenerated, activation time is 15 min), F/A-3Y-30 (activation time is 30 min), F/A-3Y-60 (activation time is 60 min), F/A-3Y-75 (activation time is 75 min), and F/A-3Y-90 (activation time is 90 minute). Fig. 4(b) shows those of the virgin GACs (Calgon 1240), GAC-5Y (GAC used for 5 years),



(a)

(b)

**Fig. 4. Variations in iodine number, specific surface area, and total pore volume.**



(a)

(b)

**Fig. 5. Relationships among loss rates, ash content, density, and total pore volume of the virgin, used, and regenerated GACs.**

GAC-5Y-15 (activation time is 15 min), GAC-5Y-30 (activation time is 30 min), GAC-5Y-60 (activation time is 60 min), GAC-5Y-75 (activation time is 75 min), and GAC-5Y-90 (activation time is 90 min). Both F/A-3Y and GAC-5Y showed similar patterns for the iodine number, specific surface area, and total pore volume. In detail, the recovery ratios for the iodine number and specific area of the regenerated GACs were 80-91% and 74-85%, respectively, compared with the virgin GACs. On the other hand, the total pore volume of the regenerated GACs was larger than that of the virgin GACs. Further, longer activation times were found to greatly increase the total pore volume. These results indicate that pore size distribution should change during regeneration. In other words, micropores (<20 Å) were changed into mesopores (20-500 Å), and mesopores were changed into macropores (>500 Å).

Fig. 5 shows relationships among the loss rates, ash contents, density, and total pore volume of the virgin, used, and regenerated GACs. The used GACs had more ash content than the virgin GACs due to the attached microorganic matter. Further, in the case of regeneration, the ash content slowly increased as the activation time was lengthened. The increase in ash content of the regenerated GACs decreased the density. The loss rate, which means the unit mass ratio of the virgin and regenerated GACs, was nearly proportional to the ash content relative to the activation time. Those values seemed to correlate to the increase in total pore volume. The iodine number slowly increased according to activation time. On the other hand, the loss rate and total pore volume increased very sharply. These phenomena indicate that determining the critical regeneration condition under which the loss rate can be minimized while simultaneously satisfying a certain iodine number threshold is necessary.

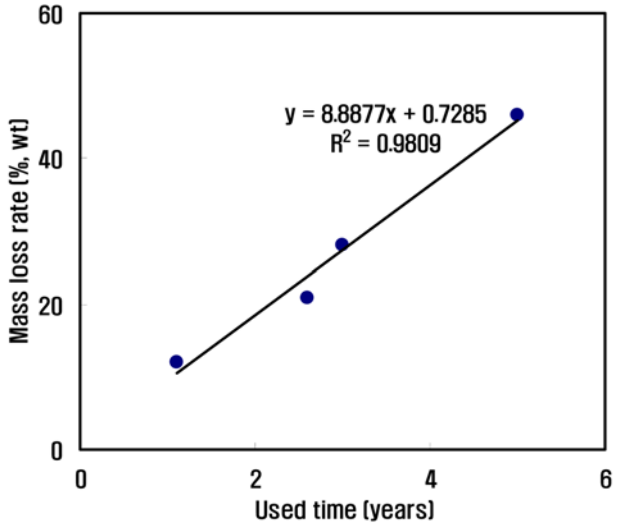


**Fig. 6. Relationship between the usage time and mass loss rate of the regenerated GACs.**

Fig. 6 shows the relationship between the usage time and mass loss rate of the regenerated GACs. The correlation equation was derived as shown in Eq. (3). This equation can be practically used for estimating the fill-up volume in a certain absorber to supply for the mass loss of GAC.

$$Y=8.89X+0.73, \qquad R^2=0.98 \tag{3}$$

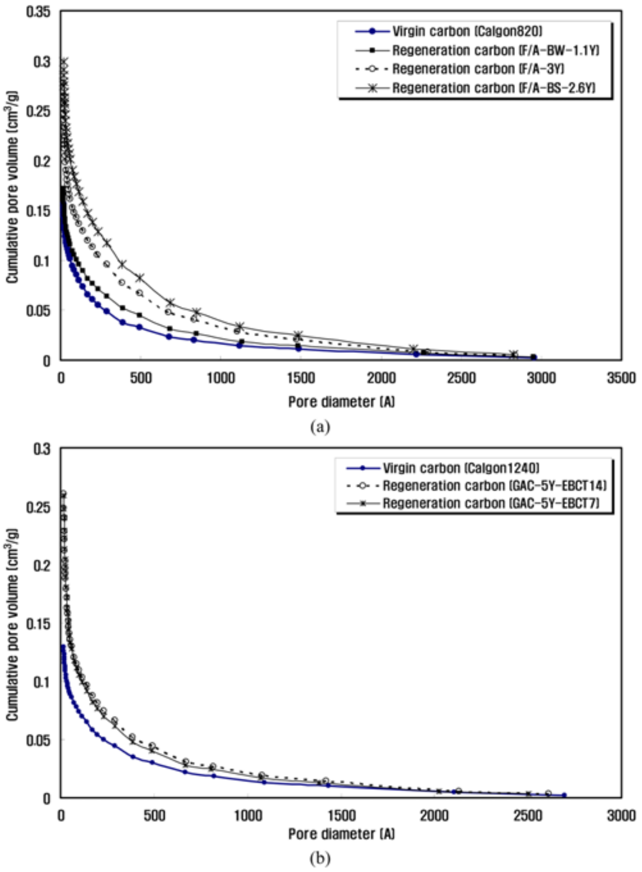


**Fig. 7. Pore size distribution and cumulative pore volumes of the virgin and regenerated GACs.**

where is the mass loss rate (%) and is the usage time.

Fig. 7 shows the pore size distribution and cumulative pore volume of the virgin and the regenerated GACs. Table 3 summarizes the variations in pore size and cumulative pore volume before and after regeneration. The regenerated GACs had higher cumulative pore volumes than the virgin GACs. In particular, the mesopore range (20-500 Å) showed a clear difference. As shown in Table 3, regeneration increased the total pore volume per unit mass but decreased the number of micropores (<20 Å). On the other hand, the numbers of macro (>500 Å) and mesopores (20-500 Å) increased. This is why the total pore volumes of the regenerated GACs were larger than those of the virgin GACs, as shown in Figs. 4 and 5.

## 2. Distributions of Inorganic Matter in the Regenerated GACs

Fig. 8 shows the distributions of inorganic matter comprising the

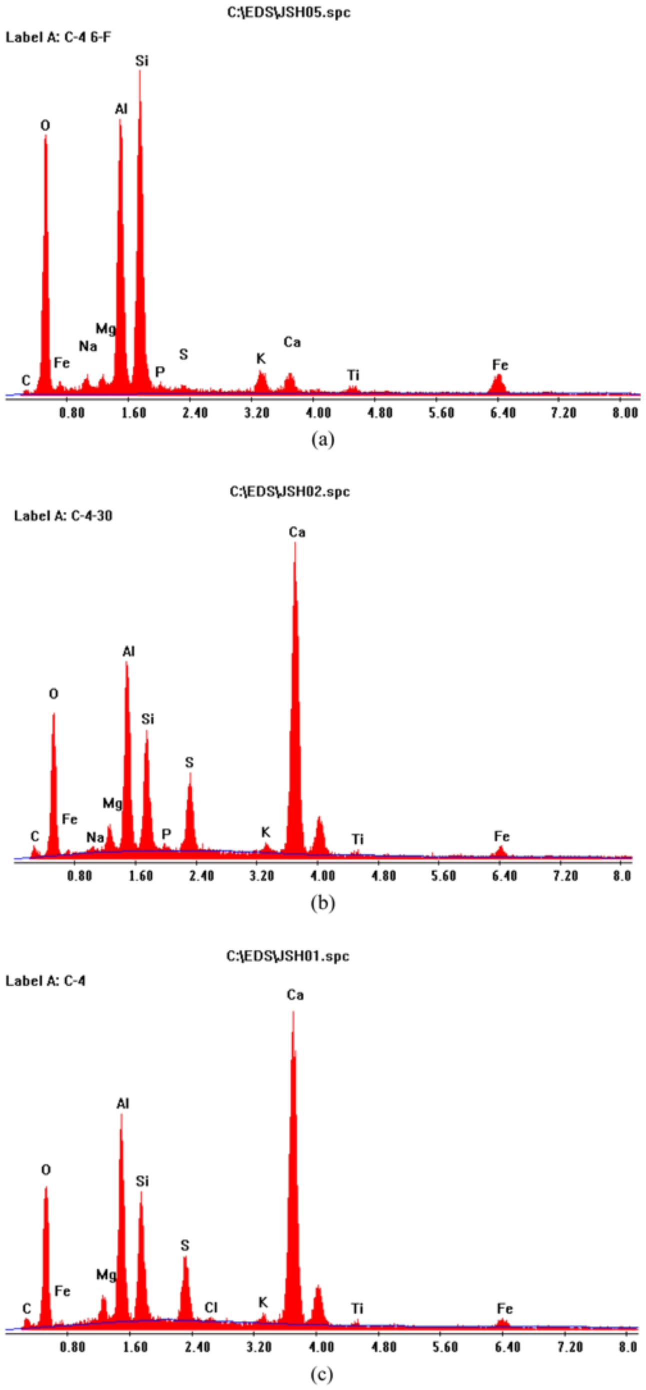


**Fig. 8. Distributions of inorganic matter comprising GACs.**

**Table 3. Variations in pore size and cumulative pore volumes before and after regeneration**

| Pore size | F/A-3Y | | | | GAC-5Y | | | |
|---|---|---|---|---|---|---|---|---|
| | Virgin (Calgon 820) (cm³/g) | Regen. (cm³/g) | Increment (cm³/g) | Percent (%) | Virgin (Calgon 1240) (cm³/g) | Regen. (cm³/g) | Increment (cm³/g) | Percent (%) |
| Total | 0.498 | 0.584 | 0.087 | 17.4 | 0.417 | 0.629 | 0.211 | 50.7 |
| Macropore (>500 Å) | 0.030 | 0.062 | 0.032 | 106.9 | 0.023 | 0.041 | 0.013 | 46.7 |
| Mesopore (20-500 Å) | 0.114 | 0.180 | 0.066 | 58.2 | 0.090 | 0.184 | 0.094 | 104.3 |
| Micropores (<20 Å) | 0.354 | 0.343 | −0.011 | −3.2 | 0.299 | 0.403 | 0.104 | 34.9 |

(a) virgin (Calgon 1240), (b) used (GAC-5Y), and (c) regenerated. Calcium (Ca) increased in the component ratios of the used and regenerated GACs relative to the virgin GAC. Fig. 9 describes the mass distribution of inorganic matter per unit mass (gram) of GACs. The mass of inorganic matter, including calcium, aluminum (Al), silica (Si), iron (Fe), and magnesium (Mg), in the used GACs was higher than that in the virgin GACs. Further, the mass increased in the regenerated GAC. In general, 5-15 wt% inorganic matter accumulates on GAC adsorbers in actual applications [8]. Other researchers previously showed that the accumulated inorganic components are quite diverse due to source water quality and the used chemicals [9].

As shown in Table 4, the ratios of ash in the virgin, used, and regenerated GACs were 4.3%, 13.6%, and 18.8%, respectively. The composition ratios grew steadily throughout the process. The composition ratios of each type of inorganic matter were converted into mass (mg) per unit gram (g) GAC to quantify them. The calcium masses were 0.9, 35.5, and 48.7 mg/g GAC in the virgin, 5-year usage, and regenerated GACs, respectively (refer to Fig. 9). Calcium is a very common matter that can be found easily in source water around the world. Moreover, it is widely used as a component of calcium hydroxide and other chemicals for water treatment. Therefore, calcium accumulation is liable to occur within the adsorption process for water treatment [10]. Calcium accumulation on GACs is important for heat regeneration because it can induce the loss of micropores as a catalyst metal.

**Table 4. Component ratios of inorganic matters**

| Inorganic matters (mg/g GAC) | Virgin (Calgon 1240) | Used (GAC-5Y) | Regeneration (GAC-5Y) |
|---|---|---|---|
| Ash (wt%) | 4.3 | 13.6 | 18.9 |
| Ca | 0.9 | 35.3 | 48.7 |
| Al | 7.5 | 16.2 | 22.7 |
| Si | 9.4 | 10.4 | 14.5 |
| Fe | 2.3 | 3.0 | 4.8 |
| Mg | 0.6 | 2.7 | 3.7 |

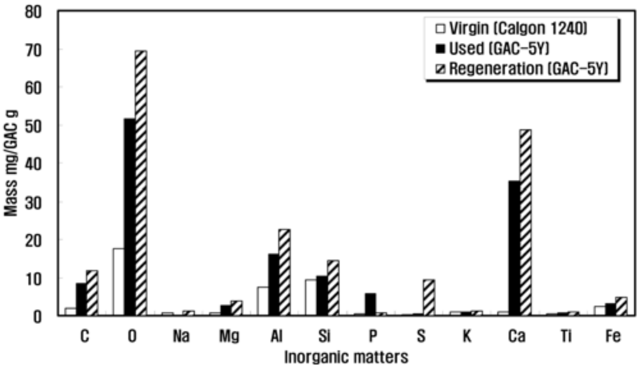


**Fig. 9. Inorganic matter mass (mg) per unit gram (g) GAC.**

### 3. Variations in Particle Size and Hardness

Since variations in particle size affect the performance of adsorption media or loss due to pulverization, GAC particle size is a very important parameter for regeneration. Table 5 and Figs. 10 show variations in GAC particle size before and after regeneration. As shown in Table 5, the maximum and minimum diameters of the virgin GAC (Calgon, 1240) were 1.69 and 0.45 mm, respectively. Those of the regenerated GAC (GAC-5Y) were 1.60 and 0.50 mm, respectively. There was little variation in the particle size before and after regeneration. These results were similar for the samples with 8×20 meshes (Calgon 820, F/A-BS-2.6Y, F/A-3Y, and F/A-BW-

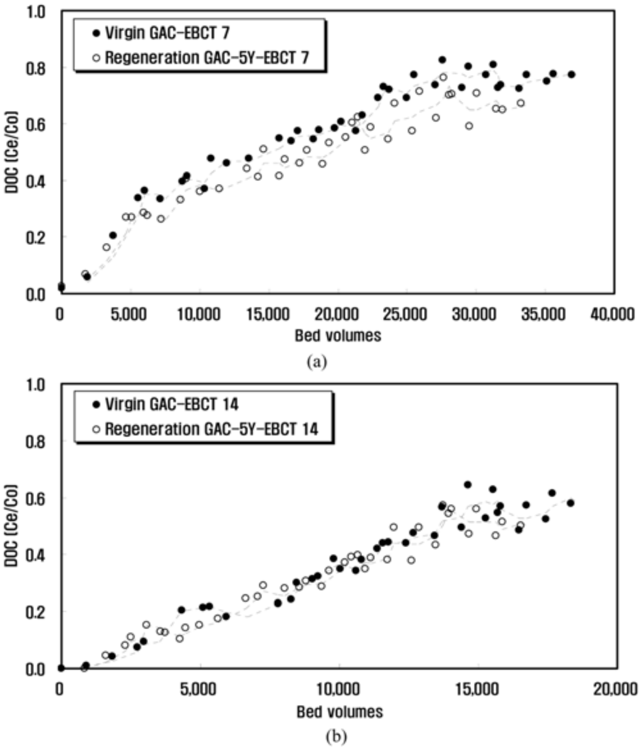


**Fig. 10. Removal efficiency of dissolved organic carbon (DOC): Co is the initial concentration of DOC, and Ce is the concentration of DOC in effluent from the columns.**

**Table 5. Particle size characteristics of the virgin and regenerated GACs**

| Division | Max. (mm) | Min. (mm) | Uniformity coefficient | Effective diameter (mm) | Hardness decreasing rate (%) |
|---|---|---|---|---|---|
| Virgin (Calgon 1240) | 1.69 | 0.45 | 1.73 | 0.64 | 98.9 |
| Regeneration (GAC-5Y) | 1.60 | 0.50 | 1.49 | 0.67 | 95.5 |
| Virgin (Calgon 820) | 1.99 | 0.86 | 1.43 | 1.03 | 94.7 |
| Regeneration (F/A-BS-2.6Y) | 1.9 | 0.52 | 1.34 | 1.02 | 97.9 |
| Regeneration (F/A-3Y) | 1.72 | 0.87 | 1.31 | 1.03 | 93.4 |
| Regeneration (F/A-BW-1.1Y) | 1.82 | 0.81 | 1.29 | 0.96 | 99.6 |

1.1Y). Even though the uniformity coefficients decreased slightly before and after regeneration, the coefficients and effective diameters did not change much. Also, it could be revealed that mechanical strength of GAC did not vary after regeneration from the fact that the hardness decreased about 4% less (refer to the last column in Table 5).

### 4. Evaluation of Adsorption Capacity

Fig. 10 shows the results of the rapid small scale column tests mentioned in the "Methods for evaluating adsorption capacity" section. It describes the removal efficiency of dissolved organic carbon (DOC) according to bed volumes (BV) under an EBCT of (a) 7 min and (b) 14 min. Filtered water taken from the rapid sand filtration process in Korea S_WTP was fed to the columns. Under the EBCT of 7 min, the removal efficiencies of the virgin and regenerated GACs were similar to each other to BV 5,000. Higher removal efficiency of the regenerated GACs for DOC than that of the virgin GACs was appeared from BV 500 to BV 35,000. Under the EBCT of 14 min, both removal efficiencies were nearly identical to BV 15,000. Although the iodine number and specific surface area did not recover to the values of the virgin GAC after regeneration, the adsorption capacity or removal efficiency for DOC was maintained. On the contrary, the removal efficiency of the regenerated GAC was 10% higher under the EBCT of 7 min. These results are because the micropores changed into mesopores after regeneration, which is more effective than the former at adsorption and DOC removal.

## CONCLUSIONS

The variations in physical properties and adsorption capacity of regenerated GACs were evaluated. The results of this study are summarized below:

1. Although the iodine number and specific surface area were not recovered to the levels of the virgin GACs through regeneration, the adsorption capacity or removal efficiency for DOC did not drop. Because the accumulated inorganic matter in the used GAC micropores was chemically changed into ash content through heat regeneration, the micropores increased in size to become mesopores (20-500 Å).

2. There was little variation in particle size and hardness before and after regeneration. Even though uniformity coefficients decreased slightly before and after regeneration, those coefficients and the effective diameters did not change much. Also, mechanical strength of GAC did not vary after regeneration from the fact that the hardness decreased about 4% less than that of the virgin.

3. The removal efficiency of the regenerated GACs for DOC was 10% higher under the EBCT of 7 min. These results were because the micropores changed into mesopores after regeneration. Mesopores are more effective for adsorption and DOC removal than micropores (<20 Å).

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