# The removal of the acetonitrile using activated carbon-based sorbent impregnated with sodium carbonate

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**Abstract**–To remove acetonitrile, various activated carbon (AC)-based sorbents impregnated with alkali or alkaline earth metal were tested in a fixed-bed quartz reactor at 30 °C. The AC-based sorbents impregnated with sodium (NaAC) showed more enhanced acetonitrile removal capacities than that of the pure AC sorbent despite a notable decrease in their surface areas and pore volumes. The NaAC-10 sorbent (with 10 wt% sodium carbonate) especially showed an excellent acetonitrile removal capacity (15 mg $CH_3CN$/g sorbent) and regeneration ability, which indicates that the alkali metal was the adsorption site of the acetonitrile.

Key words: Acetonitrile, Activated Carbon, Sorbent, Alkali Metal

## INTRODUCTION

The fluidized catalytic cracking (FCC) process is one of the most economical and efficient refinery processes for the conversion of relatively heavy hydrocarbons to lighter hydrocarbons [1-3]. $C_4$ streams of FCC units can be changed into economical products which generally contain impurities such as sulfur and nitrogen compounds [4]. Acetonitrile is the main impurity of the nitrogen compounds and is usually present at the impurity level (–15 ppmw) in the $C_4$ streams from FCC process.

$C_4$ stream may be used, after the separation of 1-, 3-butadiene and acetylenic impurities, to produce the octane boosting ethers MTBE, ETBE, TAME, and TAEE or TBA and other alcohols. The process is achieved by reaction of the most reactive components and the branched olefins isobutene and isoamylene with methanol, ethanol, or water [5-7]. These reactions occur over solid acid catalysts which most commonly belong to the family of sulfonated polystyrene/polydivinylbenzene resins. Alternatively, olefin oligomers may be produced using the same catalysts in the presence of the inactive alcohol TBA. The presence of nitriles is one of the main causes of progressive deactivation of these catalysts [8].

To remove acetonitrile in $C_4$ stream, at least three different approaches have been proposed: washing with water, selective catalytic hydrogenation, and selective adsorption on solids [5,9,10]. The water wash process can effectively remove acetonitrile. However, the supply of good-quality and plentiful water is not always available at the refinery and is therefore expected to be costly, particularly in the dry areas. Furthermore, propionitrile's lower solubility in water requires four to five times more water to be removed and reach the same low levels as acetonitrile. In the case of selective catalytic hydrogenation, much hydrogen and energy are necessary and this complicates the process. Selective adsorption on solids is one way to avoid increased costs and to save energy compared to the other process. The advantages of using sorbent (e.g., the low energy demands of the process and its potential to regenerate spent sorbents) have made the adsorption process an attractive research area. However, in the case of deep removal of acetonitrile, the research is yet considered deficient.

In the present study, AC-based sorbents were prepared via impregnation with alkali and alkaline earth metals. They were examined with the goal of developing efficient sorbents for acetonitrile below 1 ppmw. Moreover, the role of the alkali and alkaline earth metal on the surface of ACs in the adsorption of acetonitrile was discussed along with the loading amount of metal additive and with the changing physical properties of ACs.

## EXPERIMENT

### 1. Preparation of the Sorbent

The AC-based sorbents used in this study were prepared via impregnation with alkali and alkaline earth metal. First, alkali or alkaline earth metal salts such as potassium carbonate ($K_2CO_3$, Aldrich), sodium carbonate ($Na_2CO_3$, Aldrich) and calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$, Aldrich) were dissolved in water. The solution was later added to the AC (Aldrich), stirred at ambient conditions for 12 hours to allow the sorbents to age and was dried using an evaporator. After drying, the samples were calcined at 150 °C in an $N_2$ balance gas stream.

### 2. Characterization

The physical properties of the sorbents were investigated with a gas adsorption analyzer (BET), via X-ray diffraction (XRD). The specific surface area was determined through $N_2$ adsorption/desorption isotherms at 77.35 K of bath temperature, using Autosorb-1-C (Quantachrome, USA). XRD patterns of the prepared activated carbon powder samples were recorded at $2\theta$ between 10° to 80° with a multipurpose X-ray diffractometer (PANalytical, Netherlands) using the CuK$\alpha$ radiation source at 40 kV and 25 mA at the Korea Basic Science Institute (Daegu). The amount of alkali metal impregnated was identified by using inductively coupled plasma-

atomic emission spectrometry (ICP-AES: GBC Scientific, Integra KL).

## 3. Adsorption Procedures

Acetonitrile adsorption equilibrium experiments were performed in a fixed-bed quartz reactor which has 10 mm of internal diameter and 16 cm³ constant temperature section at 30 °C. The 0.1 g sorbent was packed into the reactor and treated to remove water at 150 °C in N₂ balance. The space velocity (SV) was maintained at 5,000 h⁻¹ to minimize the severe pressure drop and channeling phenomena. All volumetric gas flows were measured under standard temperature and pressure (STP) conditions. The temperature of the inlet and outlet lines of the reactor was maintained above 100 °C. The outlet gases from the reactor were analyzed automatically every eight minutes using a nitrogen chemiluminescence detector (NCD) equipped with an autosampler (Valco). The column used in the analysis was Agilent 190191J-413 capillary column. The acetonitrile adsorption and regeneration conditions are shown in Table 1.

When the acetonitrile concentration of the outlet gases reached 15 ppm, the inlet stream of mixed gases was stopped, and inert nitrogen gas was introduced to purge the system. Finally, after the adsorption of acetonitrile, the sorbent was regenerated using N₂ gas by increasing the temperature to between 30 °C and 200 °C.

## RESULTS AND DISCUSSION

### 1. Physical Properties of Various AC-based Sorbents

The physical structural properties (e.g., specific surface area, total pore volume, and average pore diameter) of various AC-based sorbents were analyzed from the nitrogen adsorption isotherm (see Fig. 1). The surface areas of AC, NaAC-10, KAC-10, and CaAC-10 were 1,393, 1,015, 1,071, and 1,211 m²/g, respectively (see Table 2). Moreover, in the NaAC series sorbents, the specific surface areas and total pore volumes were decreased by increasing the amount of sodium carbonate loading due to the impregnate aggregates on

**Table 1. Experimental conditions**

|                    | Adsorption process        | Regeneration process |
|--------------------|---------------------------|----------------------|
| Temperature (°C)   | 30                        | 30-200               |
| Pressure (atm)     | 1                         | 1                    |
| Flow rate (mL/min) | 50                        | 50                   |
| Gas composition (%)| Acetonitrile: 15 ppm      | N₂ balance           |
|                    | N₂ balance                |                      |

**Table 2. Physical properties of AC-based sorbents**

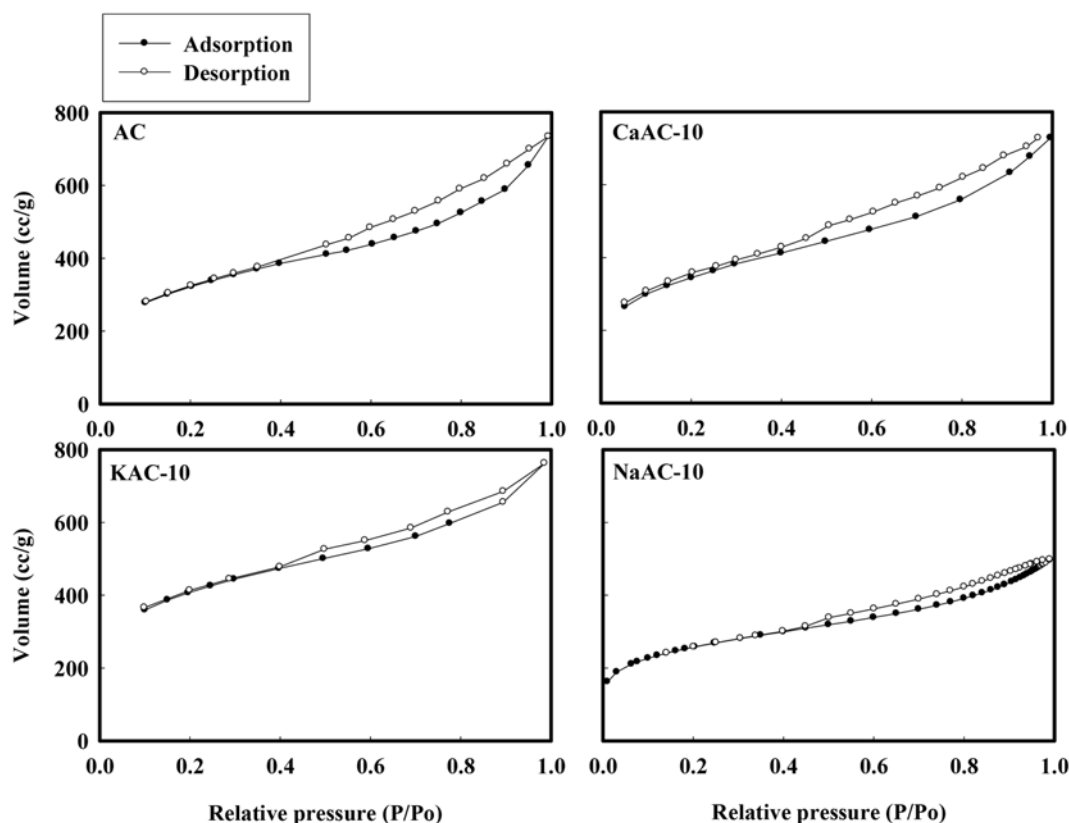| Sorbents | Specific surface area (m²/g) | Total pore volume (cm³/g) | Average pore diameter (Å) | Amount of Na₂CO₃ (wt%) |
|----------|------------------------------|----------------------------|----------------------------|-------------------------|
| AC       | 1393                         | 1.327                      | 40.72                      | -                       |
| NaAC-5   | 1296                         | 1.125                      | 34.71                      | 8.6                     |
| NaAC-10  | 1015                         | 0.771                      | 30.37                      | 11.7                    |
| NaAC-20  | 806                          | 0.477                      | 23.72                      | 21.3                    |
| NaAC-30  | 573                          | 0.420                      | 38.13                      | 33.3                    |
| KAC-10   | 1071                         | 0.924                      | 38.35                      | -                       |
| CaAC-10  | 1211                         | 1.122                      | 37.04                      | -                       |



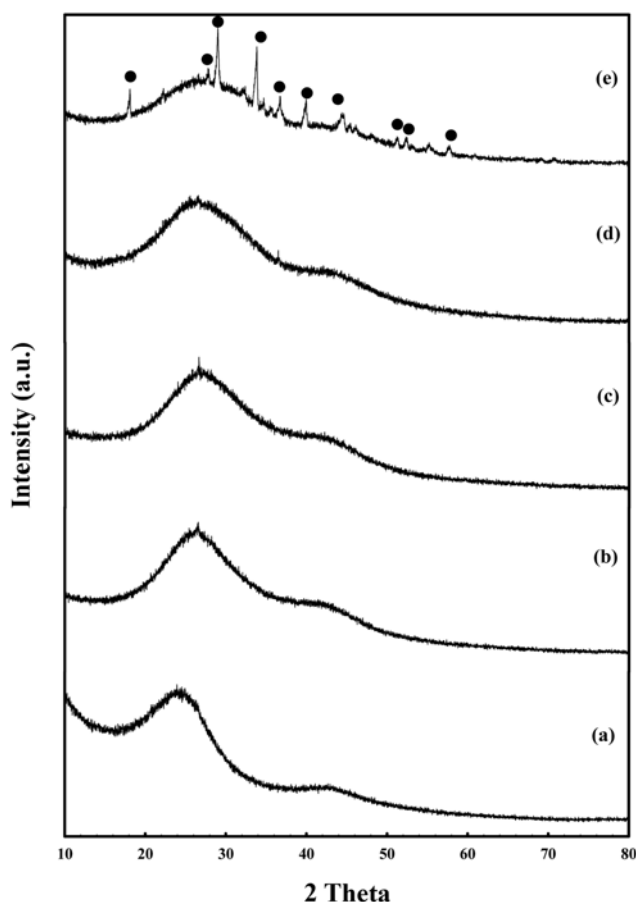Fig. 1. The adsorption and desorption isotherm curves of AC-based sorbents.

Fig. 2. The XRD patterns of the AC-based sorbents: (a) AC; (b) CaAC-10; (c) KAC-10; (d) NaAC-10; and (e) NaAC-30 (●: $Na_3H(CO_3)_2 \cdot 2H_2O$).



Fig. 3. The removal capacities of the acetonitrile of pure AC and of various AC-based sorbents (●: AC, □: NaAC-10, ◆: KAC-10, △: CaAC-10).

the internal/external surfaces; the aggregates then came to fill the pores. Table 2 shows the loading amount of $Na_2CO_3$, as investigated in the ICP-AES analysis of the fresh sorbents. The loading amount of $Na_2CO_3$ was almost proportional to the amount of $Na_2CO_3$ added in preparation of the sorbent. Fig. 2 shows the XRD pattern of various AC-based sorbents. In the case of NaAC-10, KAC-10, and CaAC-10, the crystal structure of alkali and alkaline metal was undetected. In the case of the NaAC series sorbents, the crystal structure of trisodium hydrogendicarbonate dehydrate (Trona) was observed even at 30 wt% in $Na_2CO_3$. This suggests that the sodium carbonate on the AC, below the 30 wt% loading amount of $Na_2CO_3$, exists as an amorphous material, and that above the 30 wt% loading amount of $Na_2CO_3$ was piled up on the surface of AC.

## 2. Acetonitrile Removal Capacity of Various AC-based Sorbents

The breakthrough curves of acetonitrile adsorption are the best way to evaluate the capacity of the sorbents in a typical fixed-bed experiment because the acetonitrile concentration of the outlet gas from the reactor is negligible until the entire bed is saturated with acetonitrile [12,13]. In this study, the breakthrough time was necessary to detect an acetonitrile concentration of 1 ppm in the outlet gas. Fig. 3 shows the breakthrough curves for the acetonitrile on the pure AC and the various AC-based sorbents impregnated with alkali or alkaline earth metal compound at 30 °C. The acetonitrile
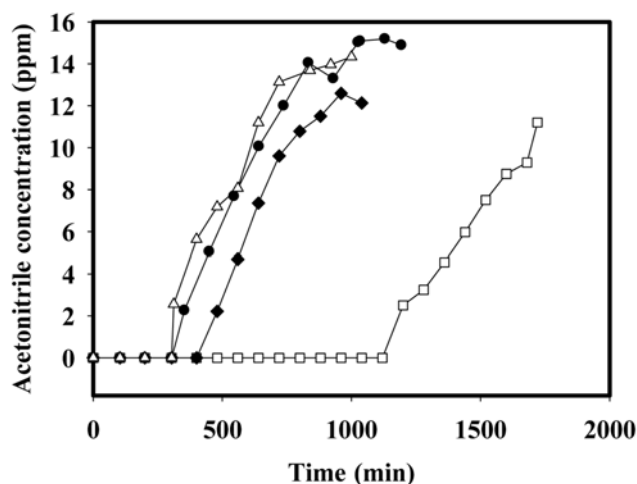
removal capacities of the AC-based sorbents were calculated until the breakthrough point. The X-axis and Y-axis indicate the adsorption time and the acetonitrile concentrations emitted from the reactor, respectively. The highest acetonitrile removal capacity until breakthrough point was found for NaAC-10. The acetonitrile removal capacities of NaAC-10, KAC-10, CaAC-10, and pure AC were 15.39, 5.50, 4.12, and 4.12 mg $CH_3CN$/g sorbent, respectively. Only sodium-impregnated AC was found to enhance the adsorption capacities of acetonitrile despite a notable decrease in the surface area of AC, as shown in Table 2.

## 3. Comparison of the Acetonitrile Removal Capacities of the NaAC Series Sorbents as a Function of the Loading Amount of Sodium Carbonate

Fig. 4 shows the acetonitrile removal capacities of the NaAC series sorbents as a function of the loading amount of sodium carbonate. The acetonitrile removal capacities of the NaAC series sorbents were increased by increasing the loading amount of $Na_2CO_3$ until 10 wt%. This result indicates that sodium carbonate was the adsorption site
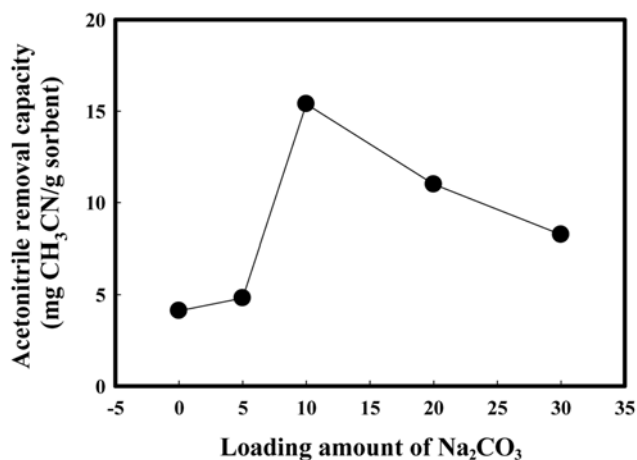


Fig. 4. The removal capacities of the acetonitrile of the NaAC series sorbents as a function of the loading amount of sodium carbonate.

of the acetonitrile even though remarkable changes in structural properties (e.g., specific surface area and total pore volume) were observed after the impregnation of different concentrations of sodium carbonate, as shown in Table 2. In the case of NaAC-10, the total pore volume and specific surface area were 0.771 cm$^3$/g and 1,015 cm$^2$/g, respectively. The performance of NaAC-10 was much higher than that of AC even though the physical properties of NaAC-10 decreased compared with those of AC. However, the acetonitrile removal capacities slightly decreased above 20 wt% of loading amount of sodium carbonate [14-16]. Considering the decrease in specific surface area and total pore volume represented in Table 2, this decreasing sorption capacity resulted from the decrease in sorption surface area or sorption sites due to the aggregation or pore blocking of sodium carbonate as the loading amount increased.

## 4. Regeneration Property of NaAC-10

The regeneration characteristics are among the most important factors to be considered in the adsorption process [17]. The spent NaAC-10 was regenerated via temperature-programmed thermal progress between 30 °C and 200 °C, using nitrogen gas. Fig. 5 shows the regeneration property of NaAC-10 during multiple cycles. When

adsorption of acetonitrile and regeneration were considered a one-cycle process, the acetonitrile removal capacity of NaAC-10 remained for three cycles (see Fig. 6). The acetonitrile concentration showed maximum peak at 95 °C and the sorbent could be completely regenerated below 200 °C. Furthermore, the regeneration property of NaAC-10 showed the same phenomena during multiple cycles.

## CONCLUSIONS

The acetonitrile removal capacity of AC-based sorbents prepared via impregnation with sodium carbonate was significantly enhanced despite a notable decrease in specific surface areas and total pore volumes. This result indicates that sodium may act as adsorption sites for acetonitrile. In the case of the NaAC series sorbents, the acetonitrile removal capacities were increased by increasing the loading amount of Na$_2$CO$_3$ until 10 wt%, but the acetonitrile removal capacities slightly decreased above 20 wt%. The decreasing sorption capacity resulted from the decrease in sorption surface area or sorption sites due to the aggregation or pore blocking of sodium carbonate as the loading amount increased. In our experimental condition, 10 wt% loading of sodium carbonate on AC was fit for the removal acetonitrile. The acetonitrile removal capacity of NaAC-10 was 15.39 mg CH$_3$CN/g sorbent, perceived to be the highest among the AC-based sorbents. Moreover, the saturated sorbents could be perfectly regenerated by increasing the temperature to below 200 °C with a N$_2$ gas stream. The acetonitrile removal capacity of NaAC-10 remained during multiple cycles. These results indicated that NaAC-10 has an excellent acetonitrile removal capacity and can be completely regenerated.
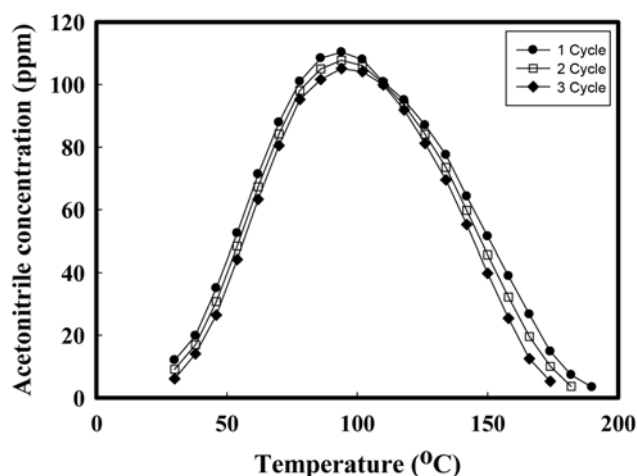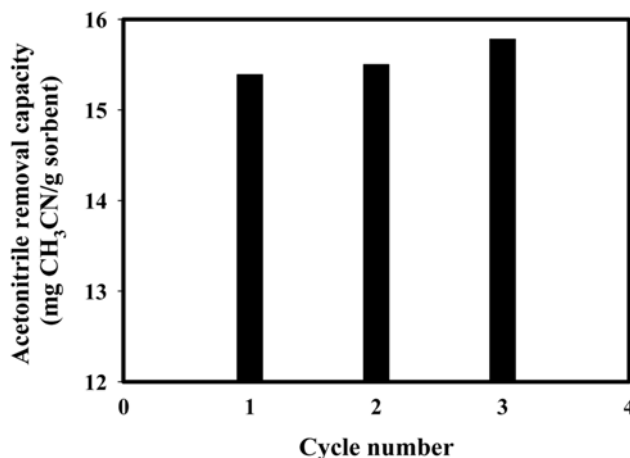
Fig. 5. The regeneration property of NaAC-10 as a function of temperature during multiple tests.



Fig. 6. The acetonitrile removal capacity of NaAC-10 during multiple cycles.

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