Chemical Adsorption of Nitrogen Dioxide with an Activated Carbon Adsorption System

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ABSTRACT

Nitrogen dioxide (NO2) is a pollutant that directly harm the human respiratory system, lead to inflammation, as well as to form the secondary aerosol pollutants. The main NO2 sources, combustion or thermal processes, were well controlled. However, the metal etching operation in semiconductor industry emits flue gases with reddish-brown NO2 fume that leads to visibility reduction, acidic odor, as well as negative effects on human health. In this study, a stream of flue gases with low NO2 (230 ± 10 ppm) and NO (50 ppm) concentrations were conducted to pass through an activated carbon-packed fixed bed for analyzing the adsorptive conversion behavior of NO2 by the activated carbon (AC) at room temperature. The repeated adsorption test was carried out by washing the regenerated waste carbon with a caustic solution and water and drying. Results propose that at the beginning of adsorption, nitrogen dioxide combined with carbon to form NO and desorbed from carbon surface. The net adsorptive conversion removal capacity of NO2 by the virgin AC and regenerated AC was 224 and 155 mg g–1 AC, respectively. Regeneration restored around 70–75% of effective surface area, pore volume, and adsorptive conversion capacity of the virgin AC. Leached caustic solution obtained from the carbon regeneration contained only nitrate and the phenomena indicates the adsorbed -C2(ONO2) hydrolyzed following the Eq. (2) -C2(ONO2) + H2O → 3 -C* + -C(O) + 2 HNO3, where -C* denotes active site on the carbon surface.

Keywords: Activated carbon; Nitrogen dioxide; Adsorption; Air pollution control.

INTRODUCTION

Nitrogen dioxide is an important pollutant in the air index. The exhaust gas generated by the metal etching operation in the TFT process has a reddish-brown color (yellow when diluted). The NO2 smoke has photochemical reactivity, which may cause acidic odor, cardiovascular effects, lung cancer, and negative health effects. (Wu and Chou, 2014; Du et al., 2017; Fang et al., 2017; Jiang et al., 2017; Xu et al., 2017; Zhang et al., 2017; Wang et al., 2018).

Techniques most commonly used to eliminate NO2 gas include selective non-catalytic reduction (SNCR), chemical scrubbing, and selective catalytic reduction (SCR). SCR and SNCR operate at gas temperatures in the range of 270–400°C and 900–1000°C, respectively, indicating they would be both better operated under high-temperature flue gas condition (Shen and Rochelle, 1998; Chen et al., 2002; Curtin, 2005; Gao et al., 2009; Chen et al., 2011; Gao et al., 2011; Gao et al., 2012; Wu and Chou, 2014; Huang et al., 2017; Liu et al., 2017; Chen et al., 2018). The most suitable method for removing NO2 and mixed acids, e.g., nitric and phosphoric, is wet scrubbing with sodium sulfide and caustic soda by the following equation: 8 NO2 + NaSH + 9 NaOH → 8 NaNO2 + Na2SO4 + 5 H2O. They are commonly used in an aluminum etching processes for producing thin film transistors-liquid crystal displayers. Unfortunately, the odor of hydrogen sulfide would further be emitted from the...
and it also has the potential to bring about other serious diseases. They observed the nitrogen dioxide adsorption on the active carbon for varying air temperatures, gas concentrations and air relative humidity. They have used parameters between 1 ppm and 30 ppm (for NO2 concentration), 23°C and 33°C (for air temperature), 30% and 90% (for air relative humidity). Results show that the humidity has not a remarkable effect on the adsorption of NO; however, increasing relative humidity causes to a decrease in the capacity of the activated carbon for NO adsorption.

The current research focuses on the performance of an activated carbon bed for NO2 adsorption and the regeneration technique of saturated carbon with a caustic solution. The washed solution was analyzed to ascertain if the adsorbed NO2 was converted to nitrite and/or nitrate ions.

**METHODS AND MATERIALS**

The experimental setup consisted of a column packed with granular activated carbon (AC) and a NOx-containing gas preparation and delivery system, as demonstrated in Fig. 1. The AC-packed column had an inner diameter of 1.0 cm and packed with crushed and screened AC for adsorption tests. The tested virgin activated carbon (ACRO-460) was supplied by ACRO Chemical Co., Taiwan. Table 1 shows the specifics of the characteristics of the original AC received. The AC was crushed, ground and screened to get a sample of fine grains with sizes in 0.84–1.00 mm. Before packing, the AC sample was conditioned in a desiccator for around 24 hours at 25 ± 2°C to get an equilibrium moisture content of about 5%. The sample was then weighted and packed into the column to a definite height for the adsorption test.

The operation conditions for adsorption tests were designed as shown in Table 2. During the first test, the effluent gas samples were analyzed half an hour for NO and NO2. The AC were eventually saturated by NO2, while the NO2 level in the effluent gas remained equal to the inlet port. After the saturation of NO2, the AC was immersed in 200 mL of an alkaline aqueous solution adjusted to pH 10 using NaOH and stirred for 14 hours to leach the adsorbed nitrate and/or nitrite. The leached AC was then filtered by a suction pump and the filtrate stored for chemical analysis. The AC was then soaked in 200 mL pure water and stirred for 2 hours to leach out the residual nitrite and/or nitrate. The 2nd-leached AC (the regenerated AC) was again filtered and the filtrate stored for chemical analysis. The regenerated AC was conditioned in the desiccator for 24 hours before being packed into the column. Because some AC was taken for analysis, mass of the AC for the 2nd adsorption test was less than the previous one (Table 2). The 2nd adsorption test lasted for 630 minutes. The virgin, exhausted virgin, regenerated, and exhausted regenerated carbon were analyzed for their surface properties, pore volume, and adsorbed oxygen contents.

A flue gas analyzer (Testo-340, Testo/Germany) was employed to determine the concentrations of NO and NO2 in gas samples. The analyzer has an accuracy of ±5%, according to the specifications supplied by the manufacturer. An ion chromatography (ICS-900, Dionex/USA) was utilized to quantify the levels of nitrite and nitrate in the filtrates obtained from the first regeneration and washing eluent.
Table 1. Some characteristics of the experimental AC as received.

| Items             | Characteristics   |
|-------------------|-------------------|
| Appearance        | Cylindrical       |
| Bulk density      | 0.4–0.5 g mL\(^{-1}\) |
| Moisture          | < 5%              |
| Iodine value      | 850 mg g\(^{-1}\) |

Table 2. Influent gas to the AC column and the operating conditions.

| Item                              | Parameters          |
|-----------------------------------|---------------------|
| Influent gas                      | NO\(_2\) 230 ± 10 ppm |
|                                   | NO 50 ppm           |
|                                   | NO\(_x\) (NO\(_2\) + NO) 280 ± 10 ppm |
| Influent gas flow rate            | 0.6 L min\(^{-1}\) |
| Operating temperature             | 25°C                |
| Inner diameter of AC column       | 1.00 cm             |
| Superficial velocity              | 0.127 m s\(^{-1}\) @25°C |
| Packed height and mass of virgin AC | 2.00 cm/0.75 g |
| Packed height and mass of regenerated AC | 1.70 cm/0.69 g |

The pH of the filtrates was measured by a pH meter (pH 526, WTW/Germany). The instrument used to analyze the surface area and pore volume of the AC sample was a BET surface analyzer (ASAP 2020 Accelerated Surface Area and Porosimetry System, Micromeritics Instrument Co., USA).

RESULTS AND DISCUSSION

**NO\(_2\) Adsorptive Removal Breakthrough Curves**

Fig. 2(A) shows NO, NO\(_2\) and NO\(_x\) (NO + NO\(_2\)) concentrations of the gas influent to and effluent from the bed packed with the virgin AC as a function of time. During the initial 210 min, there was less than 10 ppm NO\(_2\) emitted from the bed, indicating the removal efficiency of NO\(_2\) approached over 90% (as shown in Fig. 3). However, the effluent gas contained 102–196 ppm in addition to the influent 50 ppm of NO and the additional NO was converted from NO\(_2\). NO increased rapidly in the first 30 min, reached a maximum of 246 ppm at 180 min and dominated the NO\(_x\) emission before 280 min operation. Additionally, the NO\(_x\) in the influent was predominated by NO\(_2\) after 360-min operation, since the capability of NO\(_2\) adsorption of AC reduced. An approach of the influent NO\(_x\) of 280 ppm and effluent NO\(_x\) of 286 ppm at 600 min indicates that after the time, the carbon had been nearly saturated with NO\(_2\) and the conversion capability of NO\(_2\) to NO of the carbon was nearly diminished. The effluent gas had a NO\(_x\) of 282 ppm at the end (720 min) of the adsorption operation. Our finding of NO\(_2\)/NO adsorption/desorption phenomenon is similar to those observed in the study on AC treatment at 50°C for NO\(_2\), presented by Gao et al. (2011). The mechanism has been reported as follows Eqs. (1)–(6) and Fig. 4 (Gao et al., 2011):
Fig. 2. Time variations of influent and effluent NO\textsubscript{x} (NO + NO\textsubscript{2}), NO, and NO\textsubscript{2} concentrations to and from the (A) virgin AC and (B) regenerated AC columns.

![Diagram of NO\textsubscript{x} concentrations](image)

Fig. 3. Time variations of NO\textsubscript{2} removal by the AC.

![Diagram of NO\textsubscript{2} removal](image)

\begin{align}
\text{NO}_2 + \text{-C}^* & \rightarrow \text{-C(NO}_2) \text{ or NO}_2 + \text{-C}^* & \rightarrow & \text{-C(ONO)} \quad (1) \\
\text{-C(NO}_2) & \rightarrow \text{-C(O) + NO} \\n\text{-2C(O) + 2NO}_2 & \rightarrow \text{-2C(ONO}_2) \\n\text{-2C(ONO}_2) + 2\text{NO}_2 & \rightarrow \text{-2C(ONO}_3) + 2\text{NO} \\n\text{-C(NO}_2) + \text{-C(NO}_2) & \rightarrow \text{-C}_2(\text{ONO}_2) + \text{NO} \\n\text{-C}_2(\text{ONO}_2) & \rightarrow \text{2 -C(O) + NO} 
\end{align}

The NO\textsubscript{2} could be directly adsorbed/desorbed by functional group “-C\textsuperscript{*}” as Eq. (1), while the stability of adsorbed structure, -C(ONO), was not stable and tend to broken down and release one molecule of NO and form one -C(O) group (as shown in Eq. (2)). Additionally, the functional -C(O) could bind two NO\textsubscript{2} and temporarily form two groups of -2C(ONO\textsubscript{2}) (as shown in Eq. (3)). Furthermore, the C(ONO\textsubscript{2}) groups might temporarily react with extra NO\textsubscript{2} molecule and form a more stable functional group, -C(ONO\textsubscript{3}) as shown in Eq. (4). On the other hand, the Eq. (5) indicates that two adjacent -C(NO\textsubscript{2}) groups could be combined and converted to a stable -C\textsubscript{2}(ONO\textsubscript{2}), and one molecule of NO would escape from the AC surface. Eq. (6) reports that of -C\textsubscript{2}(ONO\textsubscript{2}) could be decomposed and formed -C(O) and NO, when the carbon is thermally regenerated.

Fig. 2(B) shows time variations of NO\textsubscript{2}, NO and NO\textsubscript{x} concentrations of the gases to and from the bed packed with the regenerated AC. At the start of adsorption, effluent gas had a NO concentration of 180 ppm and in which the additional 130 ppm was converted from the adsorbed NO\textsubscript{2} according to Eqs. (1) and (2). However, during the initial 90 min, there was less than 10 ppm NO\textsubscript{2} emitted from the bed, representing over 90% removal efficiency (as shown in Fig. 3), and most NO\textsubscript{x} was in the form of NO. Afterwards, NO\textsubscript{2} increased nearly exponentially and NO decreased nearly linearly with time. At the time of 360 min, rates of NO\textsubscript{2} increase, NO decrease as well as the influent and effluent NO\textsubscript{x} were nearly equal. After 480 min, the bed lost its performance for NO\textsubscript{2} removal.

**NO\textsubscript{2} Adsorptive Removal Performances**

By the data shown in Figs. 2 and 3 show time variations of NO\textsubscript{2} removal by the virgin and regenerated AC. The removal is defined by subtracting the effluent NO\textsubscript{2} concentration from the influent one and divided by the influent value. The S-shape profiles demonstrate that the adsorptive NO\textsubscript{2} removal decreased from 100% slowly to around 80% during the beginning period which lasted about 50% of the breakthrough time for both adsorption operations. The phenomena are typical for mass transfer of pollutant(s) to the carbon surface with the fluid flowing through the carbon column. For the column with a packing height of 2.0 cm or 0.75 g of the virgin AC, 50% of the packed AC has a capacity of removing 80–100% or around 90% of the influent NO\textsubscript{2}. For the adsorption test with the virgin AC, it was estimated that during the initial 360 min (removal efficiency > 20%) of the adsorption
time, the total influent NO$_2$ was 93.3 mg (= 0.6 L min$^{-1}$ × 360 min × 220 ppm × 0.001 m$^3$ L$^{-1}$ × 46 (mg m$^{-3}$)/24.5 ppm). There were 90% of NO$_2$ (84.0 mg) adsorbed. From the data, the adsorptive removal capacity of NO$_2$ by the virgin AC was estimated to be 224 mg g$^{-1}$-AC$^{-1}$. Table 2 shows that the superficial velocity for the gas flowing through the column cross-sectional area was 0.127 m s$^{-1}$ and by this velocity, the length of mass-transfer zone for the removal of 80% of the influent NO$_2$ could be estimated to be 0.5 cm.

Similarly, for the regenerated AC with a packing height of 1.7 cm, it was estimated that during the initial 240 min (removal efficiency > 20%) of the adsorption time, the total influent NO$_2$ was 59.5 mg (= 0.6 L min$^{-1}$ × 240 min × 220 ppm × 0.001 m$^3$ L$^{-1}$ × 46 (mg m$^{-3}$)/24.5 ppm). Fortunately, the 90% in average (53.6 mg) could be still removed by regenerated AC bed in certain time period before breakthrough. The adsorptive removal capacity of NO$_2$ by the regenerated AC was 155 mg g$^{-1}$-AC$^{-1}$. The regenerated AC has a capacity of about 70% as compared with the virgin one. Bazan et al. (2016) used carbonaceous adsorbents obtained from the residue after supercritical extraction of marigold subjected to physical activation and used as nitrogen dioxide adsorbents. Dry air with 1,000 ppm of NO$_2$ was passed through a column packed with the adsorbents. Results showed that the most effective adsorbent in dry conditions had a NO$_3$ sorption capacity of 29.2 mg g$^{-1}$. The capacity was far less the that obtained by the present study.

Take the whole packed AC mass, Fig. 5 shows time variations of NO$_2$ adsorptive removal capacity of both AC. Calculate capacity by dividing the cumulative mass of removed NO$_2$ by the total filled AC mass. The virgin AC had an equilibrium capacity of around 157 mg NO$_2$ g$^{-1}$ AC with the adsorption time approaching 600 min. The regenerated one had a saturation value of 113 mg NO$_2$ g$^{-1}$ AC with time approaching 420 min. As a comparison, the regenerated one had a capacity and saturation time of both 70% from the experimental data shown in Fig. 5.

Eqs. (2), 4, and (5) display that NO can be produced from
the adsorptive removal of NO\textsubscript{2} as illustrated in Fig. 2. Time variations of conversion of NO\textsubscript{2} to NO by the AC were shown in Fig. 6. The conversion was calculated by dividing the NO increase (ppm) of the effluent gas by the influent NO\textsubscript{2} concentration (220 and 230 ppm for the test with virgin and regenerated AC, respectively). At the start of operation by using the virgin AC, the conversion was 44\% and increased to a maximum of 85\% in 180 min and decreased finally to about 10\% at 720 min. By the regenerated AC, the conversion was 60\% at the start and decreased with time to about 5\% at 630 min. By the virgin AC, the new carbon had a greater ability to adsorb NO\textsubscript{2} to form “-C(NO\textsubscript{2})”, when only a part of them converted to NO and desorbed to the effluent gas. At around 180 min, it could be postulated that reactions (2), (4) and (5) dominated with NO converted from the decomposition of -C(NO\textsubscript{2}) and -C\textsubscript{2}(ONO\textsubscript{2}). After the time, there was no enough surface area available for effective adsorption of NO\textsubscript{2} and its conversion to NO thus reduced. For the regenerated AC, effective adsorption of NO\textsubscript{2} and its conversion to NO occurred in the initial 60 min. However, the AC could not convert the adsorbed NO\textsubscript{2} to -C(NO\textsubscript{2}), while the conversion reduced gradually until the end of operation.

**Characteristics of AC**

The chemical regeneration method could only recover 70\% of NO\textsubscript{2} adsorptive removal capacity. This loss could contribute to changes in specific surface area, pore volume, and oxygen content in AC material before and after adsorption (as shown in Table 3). The specific surface areas of the virgin-unused and -saturated AC were 676 and 256 and m\textsuperscript{2} g\textsuperscript{-1}, respectively. The 62\% [= (676–256)/676 × 100\%] reduction of surface area could be occupied by the oxidizing substances, such as -C(O), -C(ONO\textsubscript{2}) and -C\textsubscript{2} (ONO\textsubscript{2}), produced by NO\textsubscript{2} adsorption processes. After the washing regeneration process, the specific surface area of the regenerated AC was recovered to 551 m\textsuperscript{2} g\textsuperscript{-1} and reduced to 235 m\textsuperscript{2} g\textsuperscript{-1} after the NO\textsubscript{2} saturated adsorption. The specific surface area differences between unused and saturated AC was 316 m\textsuperscript{2} g\textsuperscript{-1} (=57\% of the initial value. The ratio of 316/420 or 75\% of the aval surface area of the virgin and the regenerated AC is near 70\% which corresponds to the ratios of capacity and saturation time as discussed in the preceding paragraph. From the results, it could be postulated that around 57–62 or 60\% of the total surface area were available and responsible for processing raw and regenerative AC.

The oxygen contents of the virgin AC increased from 3.79 to 5.09 wt.\% after adsorption, and the increase was 1.30 wt.\% which might be attributed by the adsorbed oxygen-containing species as cited in Eqs. (2)–(4). The reduction during the oxygen contents from 5.09 to 3.12 wt.\%, however, the regenerated AC did not restore its original performance due to pores and surface area volume reduction as shown in Table 3. The oxygen content of the regenerated AC after adsorption increased to 6.21 wt.\%.

Table 3 also lists pore volume of the virgin and regenerated AC before and after adsorption. Pore volume of the virgin AC reduced from 0.326 to 0.124 cm\textsuperscript{3} g\textsuperscript{-1} after adsorption, and the decrease was 0.202 cm\textsuperscript{3} g\textsuperscript{-1}. For the regenerated AC, The reduction before and after adsorption was 0.154 cm\textsuperscript{3} g\textsuperscript{-1}, 0.262 and 0.108 cm\textsuperscript{3} g\textsuperscript{-1}, respectively. The ratio of 0.154/0.202 or 76\% of the pore volume decrease is near 70\% which corresponds to the ratios of capacity and saturation time as discussed in the proceeding section. Fig. 7 shows pore volume distributions of the virgin and regenerated AC. For the virgin AC, most pores had sizes between 1.1 to 2.5 nm and the volume reduction occurred mainly in the same pore size range. The regenerated AC had similar pore size as the virgin one, however, the reduction in pore volume occurred mainly in the size range of 1.1–1.5 nm.

**Regeneration Leachate**

Table 4 shows properties of aqueous solution leached from AC regeneration. Aqueous solution from the first leaching operation by alkaline water adjusted to pH 10 turned to acidic with a pH of 2.36. The leachate from the second leaching operation by pure water was also acidic with a pH of 3.77. Nitrate was the only anion detected in both leachates. Gao et al. (2011) states that the adsorbed NO\textsubscript{2} might converted into an adsorbed form of nitrate as -C\textsubscript{2}(ONO\textsubscript{2}). Upon leaching, -C\textsubscript{2}(ONO\textsubscript{2}) hydrolyzed to aqueous nitrate and the corresponding equation might be expressed as:

\[
2\text{-C}_2(\text{ONO}_2) + 2\text{OH}^{-} \rightarrow 3\text{-C}^{*} + \text{-C(O)} + 2\text{NO}_3^{-} + \text{H}_2\text{O} \quad (7)
\]

| Activated Carbon Columns | Oxygen content, wt.% | Surface area, m\textsuperscript{2} g\textsuperscript{-1} | Pore volume, cm\textsuperscript{3} g\textsuperscript{-1} |
|--------------------------|----------------------|---------------------------------|-----------------|
| Virgin                   | 3.79                 | 676                             | 0.326           |
| Virgin after adsorption   | 5.09                 | 256                             | 0.124           |
| Regenerated              | 3.12                 | 551                             | 0.262           |
| Regenerated after adsorption | 6.21               | 235                             | 0.108           |

Fig. 6. Time variations of conversion of NO\textsubscript{2} to NO by the AC.
Fig. 7. Pore volume distributions of the (A) virgin AC and (B) regenerated AC.

Table 4. Properties of aqueous solution leached from AC regeneration.

| Liquid for regeneration | Leached water from AC regeneration |
|-------------------------|-----------------------------------|
|                         | NO$_3^-$ (mg L$^{-1}$) | pH   |
| Alkaline water          | 624                          | 2.36 |
| Pure water              | 25.7                         | 3.77 |

2 -C$_2$(ONO$_2$) + H$_2$O $\rightarrow$ 3 -C* + -C(O) + 2 HNO$_3$  \hspace{1cm} (8)

Eqs. (7) and (8) demonstrate that the adsorption site “-C*” could be regenerated by leaching the adsorbed AC by alkaline solution or water, and oxygen contents of the AC could be reduced.

CONCLUSIONS

In this study, passing the test air stream containing 230 ± 10 ppm NO$_2$ and 50 ppm nitric oxide (NO) through an activated carbon-packed bed for the purpose of studying the adsorptive conversion behavior of NO$_2$ by the activated carbon (AC) at room temperature. The regenerated carbon was regenerated by washing with a water and caustic solution, and dried to carry out repeated adsorption tests. The following conclusions can be drawn:

1. At the beginning of adsorption, two nitrogen dioxide molecules combined with two adjacent -C* (or -OC group) to form -C(NO$_2$) or -C(ONO$_2$), and release molecules of NO from the AC surface. The adjacent group of -C(NO$_2$) could further form -C$_2$(ONO$_2$) and enhance the stability of adsorbed NO$_2$.

2. The net adsorptive conversion removal capacity of NO$_2$ by the virgin AC and regenerated AC was 224 and 155 mg g$^{-1}$ AC, respectively, during the initial 50% of the breakthrough time. For the whole breakthrough time, the virgin AC had an equilibrium capacity of around 157 and 113 mg NO$_2$ g$^{-1}$ AC.

3. Regeneration restored around 70–75% of effective surface area, pore volume, and adsorptive conversion capacity of the virgin AC. Leached caustic solution obtained from the carbon regeneration contained only nitrate and the phenomena indicates the adsorbed -C$_2$(ONO$_2$) hydrolyzed following the equation 2 -C$_2$(ONO$_2$) + H$_2$O $\rightarrow$ 3 -C* + -C(O) + 2 HNO$_3$.

The positive results of NO$_2$ removal by AC column found in the current study promote the development of the real-scale equipment and need to confirm its durability. The operation and phenomenon would be significantly different in a scale-up progress for a more practical use. The real-scale equipment could include twin beds, one in operation and the other in regeneration. A regeneration process will include (1) caustic desorption of the adsorbed NO$_2$ and NO$_3$, (2) water rinsing of the regenerated carbon, and (3) drying of the rinsed carbon.

NOMENCLATURES

-C*: active site on the carbon surface.
-C(O): oxygenated carbon surface.

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