Effect of Surface Property of Activated Carbon on Adsorption of Nitrate Ion

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In this study, the removal of acidic functional groups and introduction of basic groups/sites on activated carbons (ACs) by outgassing and ammonia gas treatment were respectively carried out to enhance the nitrate ion adsorption in aqueous solution. Then, the relationships between nitrate ion adsorption and solution pH as well as surface charge of AC have become a new problem for drinking water. This problem would be attributed to low amount of nitrogen compounds used for fertilization and disposal livestock excreta. According to the investigation of the Ministry of the Environment, the Japanese government, the number of wells overrunning environmental standard for nitrate ion (44.3 mg-N/\text{L} = 10 mg-N/L) was approximately 30% for all of wells investigated. It is also indicated that the number of wells exceeding an environmental standard of nitrate ion was the highest, and has been increasing in comparison with others such as arsenic and tetrachloroethylene. 7 Nitrate ion contamination in groundwater has also been reported from other countries. Over half of the investigated sites exceeded the international standards of 50 mg-N/\text{L} for drinking water in northern Rajasthan, India. 7 In northern part of China, the more severe situation of groundwater was found out in agricultural land to be 300 mg-N/\text{L}. It is suggested that drinking water including excess nitrate ion causes methemoglobinemia for infant and generates nitrosamine, which would act as carcinogen. 1,5 Therefore, the removal method for nitrate ion would be one of the subjects on the preservation of water quality for groundwater.

So far, there have been traditional methods for the removal of nitrate ion such as the reverse osmosis and ion exchange. 6,7 However, these methods include shortcomings from the viewpoint of high running cost. On the other hand, adsorption is realized to be low cost, simple operation and widely used for water purification. Although there are several adsorbents such as zeolite and silica gel, activated carbon (AC) would be one of the typical and useful adsorbents because of porous structure, large surface area and pore volume. AC can be also prepared inexpensively from various materials and/or precursors such as biomass without any special facilities, so that AC can be used in many countries. In recent year, activated carbon fiber (ACF) has been developed as a purification material for pollutants, exhibiting several benefits such as easy operation and processing in various shape and size. Moreover, AC possesses hydrophobic surface property, thereby it is a superior adsorbent for organic pollutants compared to ionic contaminant. 8

 Recent study indicated the possibility that the adsorption capacity of AC for organic contaminant could be promoted by chemical and heating treatment introducing the functional groups on the carbon surface. Yoshihara et al. and Chen and Wu suggested that AC with large amount of acidic functional groups introduced by oxidation treatment was effective for heavy metal adsorption. 9,10 It has also been reported that the basic nitrogen-containing functional groups on the surface of absorbent introduced by ammonia gas treatment could achieve the better adsorptive removal of nitrate ion than non-treated AC. 11–13 Accordingly, it is expected that the basic groups/sites such as nitrogen-containing functional groups on the carbon surface would be effective for the adsorption of ionic substances, and that large amount of basic groups/sites could enhance the adsorption of ionic substances. However, the mechanisms of nitrate adsorption onto AC, especially the effects of equilibrium solution pH (pH_e) and the coexistent ion presented in the same solution, have not been revealed in detail. The information would be essential for making guideline of the AC to remove the nitrate ion and/or for the selection of AC in the practical use at effluent plants.

In this study, the removal of acidic functional groups and basic groups/sites on ACs by outgassing and ammonia gas treatment were respectively carried out to enhance the nitrate ion adsorption in aqueous solution. Furthermore, the relationships between nitrate ion adsorption and solution pH as well as surface charge of AC were investigated to understand the basic mechanisms of nitrate ion adsorption by AC.

Key words nitrate ion; adsorption; activated carbon; surface; removal

Effect of Surface Property of Activated Carbon on Adsorption of Nitrate Ion

In recent years, groundwater has been polluted by various kinds of organic and inorganic chemicals. In particular, the pollution of groundwater by nitrate ion has become a new problem for drinking water. This problem would be attributed to large amount of nitrogen compounds used for fertilization and disposal livestock excreta. According to the investigation of the Ministry of the Environment, the Japanese government, the number of wells exceeding environmental standard for nitrate ion was the highest, and has been increasing in comparison with others such as arsenic and tetrachloroethylene. Nitrate ion contamination in groundwater has also been reported from other countries. Over half of the investigated sites exceeded the international standards of 50 mg-N/L for drinking water in northern Rajasthan, India. In northern part of China, the more severe situation of groundwater was found out in agricultural land to be 300 mg-N/L. It is suggested that drinking water including excess nitrate ion causes methemoglobinemia for infant and generates nitrosamine, which would act as carcinogen. Therefore, the removal method for nitrate ion would be one of the subjects on the preservation of water quality for groundwater.

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Experimental

Preparation of ACs Filtrasorb 400 (F400, Calgon Carbon, Japan) was used in this study. F400 was coal-based granular AC (about 0.5–2 mm), and contained ca. 5% ash. Since F400 contained ash, the removal of ash was performed.
by deashing (DA) prior to the adsorption experiment. F400 was soaked in hydrochloric and hydrofluoric acids overnight without shaking, and washed several times with hot distilled water until the pH value in the washing solution was no longer changed. F400 was dried at 110°C overnight, and stored in desiccators. The AC obtained in this process was denoted as F400-DA.

To remove the surface acidic functional groups, F400-DA was heated to the desired temperature at 800°C in tubular furnace under a helium gas flow and maintained for 1 h. The F400-DA treated by these processes was referred to as 8OG (outgassed at 800°C, 15°C/min). For the introduction of basic groups/sites into the carbon surface, the ammonia gas treatment was performed. F400-DA was heated in tubular furnace at 800°C in tubular furnace under a helium gas flow. The atmosphere in the furnace was changed from helium to ammonia at 200°C. The temperature was raised to the set value at 800°C, and maintained for 1 h. The sample was cooled to room temperature under helium flow. The F400-DA treated by ammonia gas at 800°C (15°C/min) was indicated as 8AG.

**Properties of ACs** Surface area of the prepared ACs was obtained by the nitrogen adsorption/desorption isotherms at −196°C with the surface area and pore size analyzer (Beckman Coulter, SA-3100). The amount of surface functional groups was determined by Boehm titration method. Approximately 200 mg sample was added to the 25 mL standard solutions (0.05 M NaHCO₃, 0.1 M NaOH, 0.1 M Na₂CO₃ and 0.1 M HCl) in conical flask and agitated at 100 rpm for 4 d at 25°C. A 5 mL aliquot of NaOH, NaHCO₃ and Na₂CO₃ was separately sampled and titrated with 0.05 M HCl. For HCl solution, 10 mL of 0.1 M NaOH was added into a 5 mL aliquot of HCl, then the mixture of the solution was titrated with 0.05 M HCl. Phenolphthalein and methyl red were employed as an indicator. The former was used for the titration of Na₂CO₃ or NaHCO₃, and the latter was for titration of NaOH and for back titration of HCl. NaOH neutralizes carboxylic, lactonic and phenolic groups, NaHCO₃ neutralizes carboxylic and lactonic groups, Na₂CO₃ neutralizes only carboxylic groups and HCl reacts with basic groups/sites. Each functional group was estimated based on the change in concentration for each basic solution. The pH of the point of zero charge (pHₚzc) exhibits the solution pH at which the surface of AC shows no positive/negative charge. The dried AC (100 mg) was placed in 50 mL of NaOH solution (0.1 M NaOH) in a conical flask and agitated at 100 rpm for 4 d at 25°C. After the equilibrium pH of the solution was measured, the pH₀ values were plotted as a function of pHₚzc when the initial pH was equal to the equilibrium pH.

**Adsorption Studies** In kinetic studies, 2 g of F400-DA was added into 1 L NaNO₃ solution ([NO₃⁻]₀=200 mg/L) in 2 L flask. The flask was placed on a shaker with the agitation rate of 80 rpm at 25°C. Approximately 2.5 mL of the solution was taken at certain intervals and measured for adsorption amount (Qₑ) at each sampling time.

The adsorption of nitrate ion onto each prepared adsorbent was studied in batch experiments. Approximately 50 or 100 mg of the prepared AC was respectively added into 25 mL or 50 mL of NaNO₃ solution in conical flask and the mixture was shaken at 100 rpm at 25°C overnight. The adsorption studies of nitrate ion were obtained for each prepared AC, and made for the solutions without and with the adjustment of initial pH at 5.0. The initial nitrate ion concentration ([NO₃⁻]₀) ranged from 100 to 800 mg/L. To investigate the effect of solution pH on the nitrate ion adsorption, the NaNO₃ solutions ([NO₃⁻]₀=50 mg/L) with the pH₀ values from 2 to 12 were prepared with 0.1 M HCl or NaOH. Around 100 mg of F400-DA was added into 50 mL NaNO₃ solution, and the nitrate ion adsorption was allowed at 100 rpm overnight at 25°C. It was reported that the coexisting chloride ion inhibited the adsorption of nitrate ion onto AC. Therefore, the adsorption experiment was carried out under constant chloride ion concentration (30 mg/L) by adding 0.1 M NaCl to achieve the uniform effect of chloride ion on the adsorption of nitrate ion.

Nitrate ion was analyzed with ion chromatograph (Nippon Dionex KK, ICS-1100). The conditions for analysis were: eluent: 32 mM NaOH, flow rate of eluent: 1.0 mL/min, amount of sample introduced: 25 µL, column temperature: 30°C. The equilibrium pH of the solution was measured with pH meter (HORIBA, D-51).

**Results and Discussion** **Properties of AC** The surface area, surface functional groups and pHₚzc of the prepared ACs were shown in Table 1. In F400-8OG and F400-8AG, the acidic functional groups decreased compared to those of F400-DA, while the basic sites increased by approximately 4–5 times contrary to acidic groups. The increase in basic sites for F400-8OG and F400-8AG would be due to the reduction of electron-withdrawing acidic groups such as carboxyl groups as well as the increase in π electron density and/or oxygen-containing basic groups on the carbon surface. As oxygen-containing basic groups, chromene structures, ketone groups and pyrone-like groups are realized to act as basic sites, while Okayama et al. and Shaheen et al. reported that the ammonia gas treatment could introduce pyridine and amine nitrogen, which would also play a role as basic sites.

**Adsorption Kinetics** In order to determine the rate constant of nitrate ion adsorption, the following pseudo-first order model was applied to adsorption kinetics. The equation can be expressed as follows:

\[ \ln (Q_e - Q_i) = \ln (Q_e) - k_d t \]  

(1)

Table 1. Surface Properties of Activated Carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sₜₜ (m²/g)</th>
<th>Carboxylic (–COOH)</th>
<th>Lactonic (–COO–)</th>
<th>Phenolic (Ar–OH)</th>
<th>Basic site (meq/g)</th>
<th>pHₚzc</th>
</tr>
</thead>
<tbody>
<tr>
<td>F400-DA</td>
<td>1106</td>
<td>0.04</td>
<td>0.02</td>
<td>0.48</td>
<td>0.12</td>
<td>6.8</td>
</tr>
<tr>
<td>F400-8OG</td>
<td>1163</td>
<td>0.00</td>
<td>0.00</td>
<td>0.05</td>
<td>0.51</td>
<td>9.4</td>
</tr>
<tr>
<td>F400-8AG</td>
<td>1140</td>
<td>0.00</td>
<td>0.00</td>
<td>0.03</td>
<td>0.62</td>
<td>9.0</td>
</tr>
</tbody>
</table>

DA: Deashed F400, 8OG: outgassed F400-DA at 800°C, 8AG: ammonia gas treated F400-DA at 800°C.
where $q_e$ and $q_t$ (mg/g) are the adsorption amount of nitrate ion at equilibrium and at time $t$ (min), respectively. $k_1$ (1/min) is the rate constant of pseudo-first order model.

A pseudo-second order model is expressed in the form of

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}t$$

where $k_2$ (g/(mg min)) is the rate constant of pseudo-second order model.

The effect of shaking time on the adsorption amount of nitrate by F400-DA was shown in Fig. 1. The adsorption amount reached 85% of equilibrium adsorption amount within 3 h. At 6 h, the adsorption amount achieved almost equilibrium and hardly changed at 24 h. Table 2 showed that, although pseudo-first order model could not follow each experimental data, the approximation of each data for nitrate adsorption was well fitted by pseudo-second order model. These results indicated that nitrate adsorption would be governed by diffusion process rather than collision process. It was suggested again that shaking time of nitrate adsorption experiment could be enough within 6 h.

**Effect of pH on Nitrate Ion Adsorption** The relationship between the amount of nitrate ion adsorption on F400-DA and pH of the solution was shown in Fig. 2. Nitrate ion was hardly adsorbed at basic condition, implying that hydroxide ion would inhibit nitrate ion adsorption. On the other hand, the adsorption amount of nitrate ion was enhanced with the decrease in the equilibrium pH. As shown in Table 1, the pH_pzc value of F400-DA was 6.8. This indicates that the carbon surface is negatively and positively charged when the solution pH is higher and lower than pH_pzc, respectively. Under basic condition, nitrate ion could be hardly adsorbed on AC because of electrostatic repulsion between nitrate ion and the carbon surface. On the other hand, the adsorption amount of nitrate ion was increased under acidic condition, which would attribute to electrostatic attraction between nitrate ion and the carbon surface. However, the remarkable reduction of nitrate ion adsorption was observed with decreasing equilibrium pH from 3.0 to 2.0. At this pH range, the initial concentration of chloride ion increased from 2 to 20 mM, implying that the coexisting chloride ion would inhibit the adsorption of nitrate ion. The results obtained are consistent with those reported by Ota et al.\[16\] When the initial concentration of chloride ion was fixed at 20 mM by NaCl solution, the inhibition of nitrate ion adsorption by chloride ion was clearly found out, exhibiting that the adsorption amount of nitrate ion decreased at all pH regions compared to that obtained for the solutions without any pH adjustment. It was also reported that the adsorption amount of nitrate ion decreased in the presence of sulfate and phosphate ions.\[11,16\] Thus coexistent anion would cause competitive adsorption affecting the inhibition of nitrate ion adsorption, and this effect could be stronger\[15\] at the higher concentration of coexistent anion.

**Adsorption Isotherm of Each Prepared AC** Adsorption isotherms for F400-DA, F400-8OG and F400-8AG at the initial nitrate ion concentration from 100 to 800 mg/L were represented in Figs. 3 and 4. The adsorption experiments were carried out without pH adjustment for the solutions (Fig. 3) and with pH adjustment at pH_e 5 reflecting the pH value of the nitrate-contaminated groundwater.\[20\] (Fig. 4). The results obtained in the adsorption experiment were applied to Langmuir isotherm. The Langmuir isotherm is represented by the following equation:

$$Q_e = \frac{K_aC_e}{1 + K_aC_e}X_m$$

where $Q_e$ is the equilibrium adsorption amount (mg/g), $C_e$ is the equilibrium concentration (mg/L), $K_a$ is the equilibrium constant of adsorption (L/mg) and $X_m$ is the maximum adsorption amount (mg/g). The values of each parameter, $X_m$ and $K_a$
were shown in Table 3. The coefficient of determination, $R^2$, for the relationship between the experimental and predicted data was close to 1 for each AC, thereby the Langmuir model could be applicable to the data obtained in this study. In the condition without any pH adjustments, the $X_m$ values showed the descending order of F400-8OG > F400-8AG > F400-DA, and ranging from 9.3 to 13.2 mg/g at pH 7. On the other hand, when pH was adjusted to 5, the adsorption amounts of nitrate ion were remarkably increased for F400-8OG and F400-8AG, and the values were approximately twice higher than that for F400-DA. These results suggest that, in the pH 5 adjusted condition, only a small amount of sites of the carbon surface could be charged positively due to the limitation of protons in the solution, and that insufficient adsorption sites would result in the small amount of nitrate ion adsorption. Contrarily, the pH adjustment for the solutions would cause positive charge of carbon surface due to the accommodation of protons, attributing to the enhancement of nitrate ion adsorption. But Ota et al.\textsuperscript{16} indicated that the adsorption amount of nitrate ion decreased by 5–40% with chloride ion at 1–10 mM. In this study, chloride ion was presented at ca. 2–5 mM with pH adjustment, so that several tens of percent of nitrate adsorption amount would be inhibited for each solution (Fig. 4).

Accordingly, it is suggested that the introduction of basic groups/sites such as nitrogen- and oxygen-containing groups on the carbon surface would promote the accommodation of protons in acidic condition, and that the positively charged carbon surface could enhance the adsorption of nitrate ion in the aqueous solution.

**Conclusion**

In this study, the introduction of basic groups/sites on AC and removal of acidic groups from the AC surface were carried out through the ammonia gas treatment and outgassing to enhance the nitrate ion adsorption in aqueous solution, and the relationships between nitrate ion adsorption and solution pH as well as surface charge of AC were investigated to understand the basic mechanisms of nitrate ion adsorption by AC. The conclusion can be summarized as follows.

1) The nitrate ion adsorption depended on solution pH and the adsorption amount was promoted with decreasing pH.
2) The adsorption of nitrate ion was inhibited at pH 2, implying the possibility of inhibition effect of chloride ion for the nitrate ion adsorption.
3) The introduction of basic groups/sites on the carbon surface treated by outgassing and ammonia gas treatment would make AC surface charge positively, enhancing the adsorption of nitrate ion in the aqueous solution.

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