Removal of bromate from water using modified activated carbon
Tongmian Liu, Fuyi Cui, Dongmei Liu, Zhiwei Zhao, Zhiquan Liu, Huan Wang and Qi Zhu

ABSTRACT
Coal-based activated carbon (AC) was treated chemically with nitric acid, sodium hydroxide and ammonia, and its ability to adsorb bromate was investigated. Several techniques were used to characterize the physicochemical properties of these materials, including surface area, pH_{pzc} and Boehm titration. Results indicated that surface physical and chemical properties can influence the adsorption uptake of bromate on ACs simultaneously. Surface basicity and pH_{pzc} were both found to influence the electrostatic interactions between the bromate ions and the surface of the carbon. A correlation was found between basic groups and the adsorption capacity for bromate. The adsorption capacity of the carbon was found to be linearly proportional to the amount of basic groups on the surface. The bromate adsorption data collected from all the samples were found to fit the Toth isotherm model, indicating that the bromate adsorption process could occur on heterogeneous surfaces.

Key words | basic groups, bromate, modified carbon, physicochemical properties

NOMENCLATURE
A, B and D Toth isotherm constants
C_e Equilibrium liquid phase concentration (mg/L)
k_F and 1/n Freundlich isotherm constants
k_L, q_m Langmuir isotherm constants
k_{R}, a_R and \beta Redlich–Peterson isotherm constants
q_e Equilibrium solid phase concentration (mg/g)
R^2 Regression correlation coefficient

INTRODUCTION
In recent years, bromate in drinking water, which occurs as a by-product during ozonation of raw water containing the bromide ion, has become a growing concern. Bromate is a genotoxic carcinogen (Haag & Hoigne 1985). The World Health Organization has proposed a maximum level for BrO_3^- of 25 \mu g/L. In the USA and the European Union, the concentration of BrO_3^- in drinking water must not exceed 10 \mu g/L (Siddiqui et al. 1996). China also imposes a limit of 10 \mu g/L.

Activated carbon (AC) is widely used because of its simplicity and economy in configuration and operation (Bansal & Donnet 1988). ACs have been used to remove organic and inorganic pollutants from water (Derylo-Marczewska et al. 2012). Many studies have evaluated adsorption by both granular and powdered AC for removing BrO_3^- from water (Bao et al. 1999; Kirisits et al. 2000). Several studies have investigated the use of granular AC filtration for removal of BrO_3^- from water, and have yielded varying results, reporting poor to effective BrO_3^- removal (Siddiqui et al. 1996).

The physical and chemical nature of carbon surfaces influences their adsorptive properties (Huang et al. 2008). Investigations of carbon materials modified to increase their effectiveness are of fundamental importance. There are many articles that report on AC modified by various acids to improve removal of metal ions and organic
matter. For example, Liu et al. (2007) reported that coconut-based AC modified by nitric acid showed an excellent ability to absorb Cr(VI). Shim et al. (2001) modified pitch-based AC fibers with nitric acid; this caused the introduction of a significant number of oxygenated acidic surface groups onto the carbon surface. Siddiqui et al. (1996) modified AC with nitric acid and HCl to enhance the removal of bromate. Reduction treatment of ACs with bases for removal of metal ions and organic materials has been described in many reports. However, there have been few reports on the modification of ACs by bases for improved bromate removal. In the present work, AC was modified using nitric acid, sodium hydroxide and ammonia. Four isotherm models were used to evaluate adsorption of bromate on ACs. The effect on the physicochemical properties of AC on bromate adsorption was studied. The relationships between the basic character of the carbon surface and bromate removal are discussed in this paper.

**MATERIALS AND METHODS**

**Materials**

The carbon used in this study was coal-based. Before use, the carbon was rinsed exhaustively with deionized water to remove carbon fines and to create an invariable pH value. It was then dried at 105 °C and stored in a desiccator. The carbon is hereafter referred to as AC-NX.

**Carbon modification**

**Nitric acid modification**

One hundred milliliters of 15 mol/L concentrated nitric acid solution was introduced into a 250 ml flask and heated to 90 °C in a constant temperature thermal bath device with condenser. Then 20 g original carbon was immersed in the boiling nitric acid at 90 °C for 6 h. The modified AC was washed with deionized water to an invariable pH and dried at 105 °C for 24 h. This carbon is hereafter referred to as AC-HN.

**Sodium hydroxide modification**

About 20 g of original carbon was placed in 200 ml of 0.1 mol/L solution of sodium hydroxide and soaked for 24 h. Then the modified carbon was washed with deionized water to an invariable pH and dried at 105 °C for 24 h. It is hereafter referred to as AC-NN.

**Ammonia modification**

About 20 g of carbon was placed in 200 ml of 15% concentrated ammonia solution and soaked for 24 h. Then the modified carbon was washed with deionized water to an invariable pH and dried at 105 °C for 24 h. It is hereafter referred to as AC-NH3N.

**Characterization of carbons**

The surface area of each sample was determined from the N2 adsorption and desorption isotherms measured at 77 K using an adsorption apparatus (ASAP 2020 V3.0H, USA). The pH of the point of zero charge (pHzpc) of each sample was established using the method suggested by Noh & Schwarz (1989). The initial pH values were 3, 6, and 11 and the mass ratio of carbon versus water was in the range 0.5–15%. The content of the surface groups of the samples was determined by the Boehm titration method (Boehm 1966).

**Analysis**

BrO3− and Br− concentrations were obtained using an ion chromatograph (Model ICS-3000, Dionex) equipped with IonPac AS-19 guard columns and an anion micromembrane suppressor. A DS6 conductivity detector was employed for bromate and bromide analysis. The eluent solutions were 30 mM KOH. The minimum detection limit for BrO3− was 3 μg/L.

**Adsorption isotherm**

The equilibrium adsorption isotherms of BrO3− from a synthetic solution of AC were obtained at 25 ± 1 °C using the bottle-point approach. Various concentrations of BrO3−
solution (25–250 μg/L) were added to seven glass bottles. To each of these, a suitable dose of AC was added. A period of 24 h was found to be sufficient to reach adsorption equilibrium. The bottles were placed on a shaker table and rotated at 180 rpm at 25 °C for 24 h. Then the solution was filtered through 0.45 μm filters and the residual BrO₃⁻ concentration in liquid phase was analyzed.

Four adsorption isotherms, the Langmuir isotherm, Freundlich isotherm, Redlich–Peterson (R–P) isotherm, and Toth isotherm, were used in the study to describe the adsorption behavior of bromate on AC (Table 1). The experimental data were fitted to the four isotherm models and solved using the curve fitting toolbox included in the MATLAB software package.

Comparison of adsorption uptake on activated carbons

Suitable doses of carbon and modified carbon were introduced into 150 ml glass bottles. Then, 100 ml each of 100 μg/L, 200 μg/L, and 500 μg/L BrO₃⁻ solution were added. The bottles were placed on a shaker table and agitated for 2 h at 180 rpm and 25 °C.

RESULTS AND DISCUSSION

Carbon modification

Figure 1 shows the N₂ adsorption isotherm of the original and modified carbons. The carbons show type 1 isotherms, which are characteristic of mainly microporous carbons. Treatment with nitric acid and sodium hydroxide resulted in a decrease in the volume of N₂ adsorbed by the carbon, but there was an increase for ammonia-treated carbon. All samples except AC-NN showed hysteresis loops at P/P₀ > 0.4, which indicates a certain mesoporosity in the carbons. Table 2 lists carbon parameters, including surface area, total pore volume and mesopore volume.

The nitric acid oxidation treatment and NaOH treatment decreased the surface area of the original carbon, by 16 and 11%, respectively. The ammonia treatment increased the surface area of the original carbon by 9%. Kutics & Suzuki (1990) reported that the surface area decreased considerably due to blockage of the narrow pores by the surface oxide functional groups introduced by nitric acid treatment. Nitric acid treatment can make the pore walls of the carbons collapse and extend micropores to mesopores and macropores. The oxygen groups generated hinder the entry of N₂ into the micropores (López-Garzón et al. 2003). As a strong alkaline, NaOH damages the pore structure of carbon considerably. This is another reason why the surface area decreased after NaOH treatment. It can be observed that ammonia treatment of the sample develops the porous structure of the original carbon and causes an increase in surface area, total pore volume and mesopore volume.

### Table 1 | Isotherm models adopted in this work and their parameters

<table>
<thead>
<tr>
<th>Models</th>
<th>Non-linear form</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>[ q_e = \left( \frac{q_m k L}{1 + q_m k L C_e} \right) ]</td>
<td>Langmuir (1916)</td>
</tr>
<tr>
<td>Freundlich</td>
<td>[ q_e = k C_e^{1/n} ]</td>
<td>Freundlich (1906)</td>
</tr>
<tr>
<td>Redlich–Peterson</td>
<td>[ q_e = \left( \frac{k_t C_e}{1 + a C_e^{b}} \right) ]</td>
<td>Redlich &amp; Peterson (1959)</td>
</tr>
<tr>
<td>Toth</td>
<td>[ q_e = \left( \frac{A C_e}{B + C_e} \right)^{1/n} ]</td>
<td>Toth (1971)</td>
</tr>
</tbody>
</table>

### Table 2 | Physical characteristics of original and modified carbon

<table>
<thead>
<tr>
<th>Carbon</th>
<th>S_{BET} (m²/g)</th>
<th>V_t (cm³/g)</th>
<th>V_{meso} (cm³/g)</th>
<th>D_{mean} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-NX</td>
<td>798</td>
<td>0.353</td>
<td>0.117</td>
<td>1.927</td>
</tr>
<tr>
<td>AC-HN</td>
<td>672</td>
<td>0.341</td>
<td>0.103</td>
<td>1.937</td>
</tr>
<tr>
<td>AC-NN</td>
<td>709</td>
<td>0.352</td>
<td>0.108</td>
<td>1.925</td>
</tr>
<tr>
<td>AC-NH₃N</td>
<td>867</td>
<td>0.386</td>
<td>0.135</td>
<td>1.944</td>
</tr>
</tbody>
</table>

S_{BET}: surface area; V_t: total pore volume; V_{meso}: mesopore volume; D_{mean}: average pore width.
relative to the original carbon. The observed increases in these parameters can mainly be ascribed to the decomposition of surface functional groups from the insides of the pores, leading to pore enlargement (preferentially creating mesopores) upon ammonia treatment (Stöhr et al. 1991; Jansen & van Bekkum 1994).

Table 3 shows the surface functional groups of the original and modified carbons. The nitric acid oxidation treatment distinctly increased the content of acidic oxygen-containing groups, especially the carboxyl group. As a result, the pH_{pzc} value of the original carbon changed from 7.3 to 3.2. The oxidation treatment increased the content of carboxyl and phenol by 0.68 mmol/g, while sodium hydroxide treatment decreased the content of carboxyl by 0.01 mmol/g. Ammonia treatment increased the content of basic groups by 0.09 mmol/g. These results were mainly due to the fact that the ammonia decomposed some acidic groups, such as carboxyls, phenolic groups and lactonic groups into low molecular products such as carbon dioxide and carbon monoxide and water, which were then removed from carbon and caused electron density to rise. The alkalinity of AC increased at the same time (Faria et al. 2005). The value of pH_{pzc} changed from 7.3 to 9.3.

### Adsorption isotherms

Four isotherm models were used in this study to describe bromate adsorption on ACs. The Langmuir and Freundlich models are the most frequently used. The Langmuir model is used under the assumption of a homogenous adsorption surface and monolayer adsorption (the adsorbed layer is one molecule thick). The Freundlich model is suitable for a highly heterogenous surface. The R-P model is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentrations and is in keeping with the low concentration limit of the Langmuir model. The Toth model combines the characteristics of both the Langmuir and Freundlich models (Bilgili 2006).

The isotherms of the original carbon and modified carbons are shown in Figure 2. The fitted parameters were calculated with the help of MATLAB. The isotherm constants for all the isotherms studied and the correlation coefficients, $R^2$, with the experimental data, are listed in Table 4.

The adsorption capacity values ($q_m$) of bromate were 1.47 mg/g for the original carbon, 0.88 mg/g for nitric-acid-modified carbon and 1.09 mg/g for sodium-hydroxide-modified carbon. However, the capacity increased to 1.54 mg/g for ammonia-modified carbon. The values of $1/n$ indicate a range between 0 and 1, and a degree of non-linearity between solution concentration and adsorption (Treybal 1987). The values are below unity, which implies that the adsorption process is chemical (Al-Duri 1996). This implies that the oxidation-reduction reaction occurs between the AC and bromate. Bromate was reduced to bromide by the AC during the adsorption process. The values of $n$ for the original carbon and modified carbons were above 1, indicating favorable adsorption of bromate on four ACs (Faust & Aly 1987).

The R-P constant, $\beta$, normally lies between 0 and 1, indicating favorable adsorption. The R-P isotherm has been proposed as an equation incorporating three parameters that may be used to represent adsorption equilibriums over a wide concentration range. It can be applied either in homogeneous or heterogeneous systems due to its versatility. As shown in Table 4, the Toth isotherm fits the experimental results better than the other three models. This indicated that the Toth model is the best model describing the adsorption of bromate on the original and modified carbons, because it has the greatest $R^2$ values. It has been proven that bromate adsorption occurs on heterogeneous surfaces. This isotherm presupposes a quasi-Gaussian energy distribution. Most sites have an adsorption energy lower than the peak or maximum adsorption energy.

According to the fitting results of the study, the best isotherm models for bromate adsorption were found to be as follows (in order): Toth > Langmuir > Redlich–Peterson > Freundlich.
Comparison of amount of bromate adsorption on activated carbons

Figure 3 shows a comparison of adsorption uptake of bromate by the original and modified carbon. It can be seen that the adsorption uptake of bromate by ACs after nitric acid and sodium hydroxide treatment was reduced. The adsorption uptake of bromate increased after ammonia treatment. For bromate solutions with initial concentrations of 500 $\mu$g/L, the rates of bromate removal by AC-NX, AC-HN, AC-NN and AC-NH$_3$N were 34, 3, 20 and 52%, respectively. For bromate solutions with initial concentrations of 100 $\mu$g/L, the rates of bromate removal were 41, 35, 38 and 59%. For bromate solutions with initial concentrations of 50 $\mu$g/L, bromate removal was 61, 25, 50 and 95%. For bromate solutions with initial concentrations of 50, 100 and 500 $\mu$g/L, up to 146 $\mu$g/L bromide was removed by all types of carbon.

Different modifications changed the physical properties of the surfaces of AC. The adsorption capacity for bromate here showed some connection with the surface physical properties of AC. Nitric acid treatment and NaOH treatment reduced the surface area of the original carbon, but ammonia treatment increased the surface area. The difference in surface area between the original carbon and modified carbons partially influenced the capacity to adsorb bromate.

Although modification caused a significant effect on physical properties, the behavior of these materials in bromate adsorption may be partially attributed to their chemical surface properties. The increased adsorption uptake of bromate by ammonia-modified carbon can be partially attributed to surface electrostatic interactions, which differ at different pH$_{pzc}$ values. When the pH of the solution is lower than pH$_{pzc}$, the carbon surface showed a positive charge. In this way, it caused an attractive
electrostatic interaction between the positively charged surface and the bromate anion. When the pH value was increased, electrostatic repulsions took place between the bromate ion and the carbon surface. As shown in Table 3, the value of pH_{pzc} of nitric-acid-treated carbon was lower than the pH value of the solution (pH = 5). This indicated that the surface charge of the carbon was negative, causing repulsion between bromate and the carbon surface. The values of pH_{pzc} of the original carbon, NaOH-modified carbon and ammonia-modified carbon are higher than the pH value of the solution, indicating attractive electrostatic interactions between the carbon surface and bromate ion. In addition, the pore structure of NaOH-treated carbon was seriously damaged and its surface area was decreased, influencing the adsorption uptake of bromate. This can explain why the adsorption uptake of bromate onto NaOH-treated carbon was lower than that of the original carbon.

A correlation was found between basic groups and bromate removal (Figure 4). AC-NH_3N, which removed more bromate than other ACs, was found to possess many more basic groups than the other carbons. The least effective carbon, AC-HN, contained fewest basic groups and the most acid and carboxyl groups. There is an approximately linear correlation between bromate adsorption capacity and the number of basic groups. By regression, a linear correlation is obtained as y = -0.01127 + 0.04129x, where y denotes the bromate adsorption capacity and x denotes the number of basic groups.

Table 4 | Langmuir, Freundlich, Redlich-Peterson and Toth isotherm model constants and correlation coefficients

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Carbon</th>
<th>q_m (mg/g)</th>
<th>k_L (L/mg)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-HN</td>
<td>0.88</td>
<td>0.0031</td>
<td>0.9440</td>
<td></td>
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<tr>
<td>AC-NN</td>
<td>1.09</td>
<td>0.0042</td>
<td>0.9664</td>
<td></td>
</tr>
<tr>
<td>AC-NX</td>
<td>1.47</td>
<td>0.0064</td>
<td>0.9408</td>
<td></td>
</tr>
<tr>
<td>AC-NH_3N</td>
<td>1.54</td>
<td>0.0074</td>
<td>0.9686</td>
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</table>

<table>
<thead>
<tr>
<th>Freundlich isotherm</th>
<th>Carbon</th>
<th>k_F (L/g)</th>
<th>1/n</th>
<th>R^2</th>
</tr>
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<tbody>
<tr>
<td>AC-HN</td>
<td>0.0169</td>
<td>0.8368</td>
<td>0.9216</td>
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<tr>
<td>AC-NN</td>
<td>0.0270</td>
<td>0.8178</td>
<td>0.9454</td>
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<tr>
<td>AC-NX</td>
<td>0.0417</td>
<td>0.7794</td>
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<tr>
<td>AC-NH_3N</td>
<td>0.0587</td>
<td>0.7687</td>
<td>0.9572</td>
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<table>
<thead>
<tr>
<th>Redlich-Peterson isotherm</th>
<th>Carbon</th>
<th>K_R (L/g)</th>
<th>a_R (mg/g)</th>
<th>b_R</th>
<th>R^2</th>
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<tr>
<td>AC-HN</td>
<td>0.0106</td>
<td>0.00068</td>
<td>0.6543</td>
<td>0.9441</td>
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<tr>
<td>AC-NN</td>
<td>0.0168</td>
<td>0.0018</td>
<td>0.6231</td>
<td>0.9408</td>
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<tr>
<td>AC-NX</td>
<td>0.0231</td>
<td>0.0035</td>
<td>0.5876</td>
<td>0.9401</td>
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<tr>
<td>AC-NH_3N</td>
<td>0.0356</td>
<td>0.0015</td>
<td>0.5541</td>
<td>0.9686</td>
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<table>
<thead>
<tr>
<th>Toth isotherm</th>
<th>Carbon</th>
<th>A (mg/g)</th>
<th>B (mg/L)</th>
<th>D</th>
<th>R^2</th>
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<tbody>
<tr>
<td>AC-HN</td>
<td>507</td>
<td>9911</td>
<td>1.971</td>
<td>0.9519</td>
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<tr>
<td>AC-NN</td>
<td>219</td>
<td>9917</td>
<td>1.796</td>
<td>0.9722</td>
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<tr>
<td>AC-NX</td>
<td>341</td>
<td>9915</td>
<td>1.862</td>
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<tr>
<td>AC-NH_3N</td>
<td>387</td>
<td>6935</td>
<td>1.811</td>
<td>0.9716</td>
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</table>

Figure 3 | Comparison of bromate removal by original and modified carbon.
CONCLUSIONS

Coal-based AC was modified by nitric acid, sodium hydroxide and ammonia. The nitric acid treatment was found to give rise to a large increase in the number of surface acidic groups. Correspondingly the value of pHpzc decreased. Sodium hydroxide treatment was found to decrease the number of carboxyl and lactone, and increase pHpzc. Ammonia treatment increased the number of basic groups, which caused the basicity and pHpzc to increase. The surface basicity and pHpzc were found to influence the electrostatic interactions between the carbon surface and bromate ions. Ammonia and NaOH treatments caused attractive electrostatic interactions between the carbon surface and bromate ion, while nitric acid caused repulsion.

The ability of carbon to remove bromate was found to be well correlated with the number of basic groups on the surface of the AC. The bromate adsorption capacity was found to be linearly proportional to the number of basic groups on the surfaces of the AC.

Because AC showed increased adsorption capacity for bromate after ammonia treatment, ammonia modification is here suggested as a possible modification for improved control of bromate in water.

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