Development of ion-exchange properties of bamboo charcoal modified with concentrated nitric acid

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Abstract. The surface chemistry and the structural properties of activated carbon can be altered by the acidic modification. The objective of this study is to investigate the changes occurring in bamboo charcoal (BC) during activation with concentrated nitric acid. Low temperature (500°C) carbonized BC has been prepared and oxidized with 70% concentrated boiling nitric acid (BC-AC). The porous properties of the BC are analyzed with nitrogen adsorption isotherm at 77 K. The surface structure is observed by Field emission scanning electronic microscope (FESEM) and the surface functional groups are examined by Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and the pH of the point of zero charge (pH_{ZPC}). The results reveal that severe oxidation with HNO₃ considerably decreases the surface area of BC with enhanced pore widening and FESEM observation demonstrates the erosive effect of oxidation. The FTIR analysis detects that some absorption bands are assigned for carboxyl, aldehyde and ketone groups on BC-AC. The XPS analysis also clearly shows that the ratio of oxygen and acidic functional groups has been enriched significantly on the BC-AC. The low pH_{ZPC} value of BC-AC confirms that the surface is highly acidic for the fixation of acidic functional groups on surface. In general, the existence of the abundant amount of acidic functional groups on adsorbents enhances the sorption of heavy metals ions in aqueous solution. Therefore, it is strongly expected that the modified BC, activated under the proposed conditions would be a promising ion exchanger in aqueous solution and can be applied for the adsorption of different heavy metal ions and radioactive materials from effluent.

1. Introduction
Activated carbon had been used in the field of water and contaminated water purification over the years for the uptake of a wide range of contaminants dissolved in wastewater due to the reason of its highly porous structure. Large external area, pore volume, and pore dimensions scattering are strongly interconnected to the adsorption capacity of activated carbon [1]. In general, adsorbents are physically modified by heating under a determined atmosphere and under high temperature to enhance the creations of more micropores and mesopores which are important for physisorption [2]. Moreover, acidic functional groups are spoiled and increased basicity on the carbon surface at elevated temperature. On the other hand in chemical modification process, adsorbents are soaked into certain chemical solutions to generate surface functional groups for chemisorption [3]. Chemical modification is usually more effective and economically viable for the adsorption of metallic ions compared to the activation through heating at higher temperature.

The principal objective of the chemical oxidation of carbonaceous materials is to develop the acidic functional groups on the external surface that possess ion-exchange properties in the adsorption
process. A number of chemicals have been used as oxidizing agents such as nitric acid, sulfuric acid, sodium hypochlorite, hydrogen peroxide, phosphoric acid, potassium permanganate etc. [4-6]. Different functional groups such as acidic, basic and neutral are generated due to the activation of these chemicals. Among the different chemical treatments, HNO$_3$ oxidation is commonly used in order to upsurge the total surface acidity and surface acidic functionalities [7]. Acidic functional groups are produced when surface of the activated carbon is oxidized. Adsorption of metal ions or polar substances such as agricultural chemicals from aqueous solution may be associated with the ion exchange mechanism with adsorbents. Acidic functional groups on the modified carbon may perform as ion exchangers and enhance the adsorption though modifying its selectivity to metal cation species in aqueous solution [8]. Radovic et al [9] also proposed that the acidic modification makes the donor-acceptor complexes that are positioned on the larger micropore. Their intensity on the surface of modified carbon favors the adsorption process. The specific acidic functional groups are basically important for the uptake of heavy metals and alkali earth metals cations for the reason of their chelating capability. This phenomenon can be demonstrated from the following equation [10].

$$\text{M}^{n+} + n(\text{-COOH}) \leftrightarrow (\text{-COO}) \text{nM} + n\text{H}^+$$

The reaction takes place for the reason of cation exchange mechanism where the metal cations exchange with the hydrogen of carboxylic groups. The generation of more number of acidic groups can be promoted to exchange the higher number of cations during adsorption process.

However, activated carbon is generally prepared from the non-natural sources of coal which can inhibit its uses in future. Hence, further research is deserved to introduce renewable adsorbents for sustainable use in the field of wastewater treatment. Bamboo is eco-friendly, naturally abundant, renewable and an inexpensive bioresource; mostly found in south-east Asian countries. In recent years, bamboo charcoal has attracted a great deal of attention as an adsorbent substance for the adsorption of different contaminants from polluted and drinking water due to its exclusive micro porous structure and 4 to 10 times greater surface area than those in wood charcoal [11, 12]. Therefore, the use of bamboo charcoal has increased remarkably in the adsorption of a large variety of heavy metals [13, 14]. Proper oxidation of bamboo charcoal can make it one of the most selective ion exchangers by developing of the acidic functional groups on its surface and this property can be applied successfully in wide range of purposes as an adsorbent. This paper presents the partial work of our research in this area. The objective of this study was the preparation and characterization of concentrated boiling nitric acid modified-bamboo charcoal. The changes of physiochemical properties of the bamboo charcoal upon the treatment were investigated by nitrogen adsorption, Field emission scanning electronic microscope (FESEM), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS). The acidic surface behavior was determined through the pH of the point of zero charge (pHzc).

2. Materials and methods
The preparation and surface modification of the bamboo charcoal are briefly presented below.

2.1. The procedure of bamboo charcoal preparation
Properly dried mosso bamboo (Phyllostachys pubescens) was cut into small pieces. Bamboo chips were carbonized at 500°C for 3 h with a heating rate of 5°C per min under nitrogen (N$_2$) gas flow of 150 cm$^3$/min in a muffle furnace (Yamato FP32, Japan). Carbonized bamboo charcoal was crushed by a ball mills machine (Mixer Mill MM 400, RETSCH, Japan) and sieved at about 75 μm. The obtained raw bamboo charcoal was identified as BC.

2.2. Surface modification
Raw BC was chemically modified by using 70% concentrated nitric acid. 10 g of dried BC was allowed to boil at 120°C in 100 ml HNO$_3$ (solid liquid ratio=1:10) for 6 h in a hot plate and washed carefully several times with deionized ultrapure water (Elix Millipore, Japan) using a vacuum filter for
several times until the pH was unchanged. Modified BC was oven dried at 110°C for 12 h and this was identified as BC-AC.

2.3. Characterization methods
The different physical properties analyzing methods that were used in this study are briefly presented below.

2.3.1. Surface area and porosity analysis. Physical characterization such as specific surface area, pore dimension and average pore size of BC and BC-AC were estimated based on the nitrogen gas (N₂) adsorption-desorption isotherms at -196°C (77 K). The analysis was carried out by using BELSORP-mini II, Japan according to the BET (Brunauer, Emmett and Teller) methods [15]. The total pore volume was analyzed at a relative pressure of 0.99. Before to the analysis, BC and modified BC samples were outgassed at 120°C for 3 h in the presence of nitrogen gas (N₂) flow to remove impurities adhered onto the surface.

2.3.2. Field emission scanning electron microscope (FESEM). The surface physical properties and porous structure were observed by using an Ultra-high resolution field emission scanning electronic microscope (UHR FE-SEM, model: SU8000, HITACHI, Japan). All images were taken at accelerating the voltage of 1.0 kV.

2.3.3. Fourier transform infra-red (FTIR) spectroscopy analysis. In order to understand the characteristics of surface functional groups, BC and BC-AC samples were investigated by using a FTIR spectrometer (Model: FT/IR-620, JASCO, Japan) in potassium bromide (KBr) pellet method. Properly dried samples were amalgamated with KBr powder maintaining the ratio of 1:100 (weight ratio of samples to KBr). After grinding the samples into homogenous powder, thin pellets were prepared for spectrum analysis. The absorbance of IR spectra was recorded from 4000 to 400 cm⁻¹.

2.3.4. X-ray photoelectron spectroscopy (XPS) analysis. The XPS analysis was performed to identify the elemental composition (carbon, oxygen and nitrogen), types of acidic functional groups and also their relative percentage on the surface of BC and BC-AC. The XPS spectra were obtained using an AXIS-ULTRA^{DL} instrument (Shimadzu, Japan). A monochromatic X-ray source (Al Kα, hv = 1486.6 eV) and a discharge source (He I, hv = 21.2 eV) were used during the analysis. The base pressure of the analysis chamber was about 5 × 10⁻⁹ mbar. Wide scan spectra in the 1000-0 eV binding energy (BE) range were recorded with pass energy of 50 eV for the samples analysis.

2.3.5. pH at the point of zero charge (pH_{PZC}). The pH at the point of zero charge (pH_{PZC}) of the BC and BC-AC was measured following the procedure depicted by Yang et al [16]. Briefly, a solution of 0.005 M CaCl₂ was boiled to remove CO₂ and then cooled to room temperature. The different initial pH values of the six solutions (2.0, 4.0, 6.0, 8.0, 10.0, and 12.0) were adjusted by adding 0.1 M NaOH or HCl. 60 mg of samples were put into 20 ml of the pH-adjusted solution into 100 mL Erlenmeyer flasks and allowed to equilibrate for 24h at 20°C (± 1) in a reciprocating shaker (EYELA Multi shaker MMS–3010, Japan) at 140 rpm. The final pH was recorded and a diagram was plotted between the final pH against the initial pH. The crossing point of the plotted curve and the pH_{initial} = pH_{final} line is considered as pH_{PZC}.

3. Results and discussion
The analytical results obtained through the different physicochemical study of BC and BC-AC and their relevant explanations are given below.

3.1. Porosity and surface area analysis
Textural properties including surface area, pore size distribution, and pore volume are essential
characteristics of adsorbents. The surface physical parameters of BC and BC-AC attained from the nitrogen adsorption isotherms are presented in table 1. The results demonstrate that the BET surface area, total pore volume and pore dimension reformed remarkably for the reason of the boiling nitric acid treatment. In comparison with BC, the BET surface area and pore volume of BC-AC declined from 312.50 m²/g to 2.27 m²/g and 0.1518 cm³/g to 0.0079 cm³/g, respectively. However, the calculated average pore size increased significantly from 1.94 nm for BC to 13.96 nm for BC-AC. The results suggest that the boiling nitric acid could shrink the surface area and pore volume. During nitric acid treatment some oxygen containing functional groups were introduced on the BC and this may have mainly blocked the pores and decreased the micropore volume of BC-AC [17]. Moreover, Molina-Sabio et al [18] reported that the deposition of acidic groups on the entrance of the pores in the treated activated carbon could increase the weight up to 6 to 13 % depending upon the materials and the treatment conditions. However, the widening of the pore size of BC-AC indicates that the effective action of HNO₃ causes significant damage to micropores of their structure and changes the surface area and also the pore volume [19]. Therefore, it can be concluded that liquid phase boiling nitric acid oxidation leads to fixation of acidic functional groups on modified BC surface and in the same time the partial destruction of porous structure has been occurred. It is to be expected that the modified BC enriched with oxygen–carbon groups on surface might have an enhanced affinity for chemisorption.

| Samples name | Surface area (cm²/g) | Total pore volume (cm³/g) | Avg. pore size (nm) |
|--------------|---------------------|-------------------------|-------------------|
| BC           | 312.50              | 0.1518                  | 1.94              |
| BC-AC        | 2.27                | 0.0079                  | 13.96             |

The N₂ adsorption isotherms at -196°C (77 K) of BC and BC-AC are presented in figure 1. The nature of the isotherms curve was analyzed by using the IUPAC classification [20]. The character of the adsorption isotherm generally represents qualitative information on the adsorption mechanism and porous structure of the adsorbents. It is observed that the isotherm shape of BC increases at low relative pressure and tends to plateau even at high relative pressure. In this case, after filling the micropores of the BC with N₂ gas, there was no further increase in the isotherm curve. This shape clearly indicates the Type I isotherm on the basis of IUPAC classification. This type of isotherm actually demonstrates materials characterized with microporous arrangement. On the other hand, the
shape of the isotherm of BC-AC slightly increases with relative pressure and that indicates the loss of micropores on the surface. Therefore, N2 adsorption isotherm of BC-AC can be considered Type II isotherm which generally focuses on the non-porous or macro-porous material.

3.2. FESEM observations

Figure 2 demonstrates the morphological image of raw and modified bamboo charcoal. It can be obviously perceived that the surface of BC is highly porous in structure and pores are well developed. However, the surface morphology of the BC was modified due to the nitric acid oxidation. In the BC-AC sample, it can be observed that the porous structure of the surface almost disappeared due to clogging. This phenomenon may have led to the reduction of the surface porous structure which is already proved by the surface area analysis.

![Figure 2. FESEM images of (a) BC and (b) BC-AC.](image)

3.3. FTIR analysis

In the chemisorption process, adsorption of cations is generally enhanced by the existence of the higher amount of acidic functional groups on the adsorbent surface. FTIR analysis is important for qualitative postulation of the nature of functional groups [21, 22]. FTIR spectra for raw and modified BC were presented in figure 3 and the changes and formation of new spectra were discussed. There are some IR spectra that were shifted; extruded and new peaks were formed on the modified BC compared with raw one.

The weak spectra in the broad region of 3413.39 cm\(^{-1}\) and 3667.94 cm\(^{-1}\) on BC are related to hydroxyl groups (–OH) that were shifted in 3444.24 cm\(^{-1}\) and 3744.12 cm\(^{-1}\) on BC-AC, respectively. Moreover, a small bending vibration in 3856.93 cm\(^{-1}\) and 2481.94 cm\(^{-1}\) on BC-AC were attributed due to the appearance of the same type of functional groups [23].

The most important peaks were formed at 1711.61 cm\(^{-1}\), and 1611.23 cm\(^{-1}\) region on BC-AC for the presence of carboxylic acid (–COOH), aldehyde, and ketone (C=O) functional groups, respectively. Haneyeh et al [24] reported that they observed the carboxylic and ketone groups in 1711 cm\(^{-1}\) and 1638 cm\(^{-1}\) region on nitric acid modified-carbon nanotubes. The same clarifications were also noted by Sellitti et al [25] and, Shim et al [17] for HNO\(_3\) oxidized activated carbon. Furthermore, the medium peak or stretching vibration on BC in the region of 1593.88 cm\(^{-1}\), 1376.93 cm\(^{-1}\), and 1249.65 cm\(^{-1}\) are the characteristic of carbonyl groups, single C-H bond and alcohol or ester groups that were shifted after nitric acid modification in 1535.06 cm\(^{-1}\), 1339.32 cm\(^{-1}\), and 1240.97 cm\(^{-1}\), respectively.

However, in finger print region (below 1000 cm\(^{-1}\)), some minor peaks for alkene (C-H) bending were moved where adsorption process could not be clearly allocated for specific stretching vibration because of their complex relating vibration structures [26]. The possible elucidation of the alteration in a spectra, reduction, and vanishing of peaks might be due to the fact that the strong oxidation changes their surface chemistry.
Figure 3. FTIR Spectra of BC and BC-AC.

3.4. XPS analysis

XPS analysis has been used to estimate the surface chemical features of BC and HNO₃ modified BC. The surface chemical composition and functional groups which have attained from XPS analysis is shown in Table 2. According to the results, the HNO₃ treatment reduced the ratio of carbon composition significantly from 90.31% to 68.48%. However, it was surprising to see that about 228% oxygen was introduced onto the surface after concentrated acidic treatment. In addition, the percentage of nitrogen was also increased significantly from 0.39% to 1.0% on the surface of modified BC. The change of C, O, and N after modification of BC is also clearly observed in the spectra of the samples (figure 4). The decrease of carbon and rise of the surface oxygen may be due to the damage of carbon surface from severe oxidation with nitric acid. Importantly, development of surface oxygen on BC may lead to increase of the oxygen-containing surface complexes that can enhance the ion exchange properties during adsorption. It should be noted that XPS analysis can only estimate the sample structure over a depth of few nanometers.

Table 2. The percentage of elements and acidic functional groups on the surface from XPS results.

| Samples    | C     | O     | N     | Graphite | C-C   | C-O   | C=O   | COO⁻   | π-π*  |
|------------|-------|-------|-------|----------|-------|-------|-------|--------|-------|
| Peak (eV)  | -     | -     | -     | 284.4    | 285.0 | 286.5 | 288.0 | 288.9  | 290.2 |
| BC (%)     | 90.31 | 9.30  | 0.39  | 71.12    | 4.98  | 15.09 | 0.52  | 2.70   | 5.59  |
| BC-AC (%)  | 68.48 | 30.52 | 1.00  | 40.20    | 32.76 | 10.58 | 6.79  | 6.86   | 2.80  |

The high-regulation spectra of C1s were presented for further analysis using a curve fitting procedure. Deconvolution of C1s spectra represents six peaks of surface functional groups at different binding energy (BE) as reported [25, 26]. These are graphitic carbon (284.4 eV), C-C (285.0 eV), C-O (286.5 eV), C=O (288.0 eV), COO⁻ (288.9 eV), and π-π* (290.2 eV). These groups are illustrated in figures 5(a) and 4(b) and the percentage of each group is listed in table 2.
Figure 4. Acidic functional groups from XPS analysis for (a) BC and (b) BC-AC.

Figure 5. XPS spectrum of BC and BC-AC with their C1s, O1s and N1s % atomic concentration.

Figure 6. pH_{PZC} of BC and BC-AC.

The results revealed that a great quantity of the carbon atoms on the surface is graphite configuration. C-O is the predominant essential of oxygen holding functional groups. The surface modification leads to increase in the substantial portion of aldehyde/ketone (C=O) and carboxyl (COO\(^-\)) groups at 0.52 % and 2.70 % in BC to 6.79 % and 6.86% in BC-AC, respectively. Similar results were also experienced for HNO\(_3\) modified activated carbon by Chen and Shunnian [29]. It can be estimated that the significant growth of oxygen holding functional groups (C=O and COO\(^-\)) on the BC surface can be introduced it as a auspicious adsorbents to uptake heavy metals and radioactive materials from aqueous solution by ion exchange process.

3.5. pH at the point of zero charge (pH_{PZC})

The pH at the point of zero charge of adsorbents indicates the chemical and electrical potential of the functional groups on solid surface [8]. Generally, the surface charge of the adsorbents is positive when the pH of the adsorbate solution is lower than the pH_{PZC}. Positive charged surface always inhibited the attraction of metal cations from the adsorbate solution because of the repulsive force between protons and metal cations. Figure 6 shows that the pH at the point of zero charges of BC and BC-AC. The pH_{PZC} of raw BC and modified BC were 10.20 and 2.10, respectively. Therefore, BC and BC-AC might have enhanced adsorption capability of cations at above their pH_{PZC} value. Furthermore, the
extremely low pH_{PZC} on BC-AC might be the reason of the deposition of sufficient acidic functional groups on the surface during oxidation.

4. Conclusions
Activation of BC with concentrated nitric acid is one of the promising approaches to produce oxygen containing functional groups on adsorbents although it can damage their textural properties. In our study, low temperature carbonized BC was activated with concentrated boiling nitric acid. The results demonstrated that a huge number of oxygen containing surface functional groups deposited on the modified BC surface. In FTIR analysis, results showed that new adsorption peak for carboxylic and aldehyde/ketone groups were generated on the surface. Moreover, XPS results also clearly exhibit that a higher percentage of carboxylic and aldehyde/ketone functional groups developed on BC-AC. The pH at the point of zero charge (pH_{PZC}) of BC-AC indicated that its surface was strongly acidic due to the deposition of acidic functional groups on surface. These acidic functional groups could generally improve the ion exchange capacity of modified BC. Therefore, it can be strongly expected that the modified BC under the proposed conditions would be a promising ion exchanger in aqueous solution. It is also estimated that the modified BC could be applied to the adsorption of different heavy metals and radioactive materials from wastewater and drinking water. The use of this adsorbent for the removal of such cations would be really interesting in practice. Recently our research group used this adsorbent for the adsorption of cesium from aqueous solution. The obtained results reveal that about 100% of cesium is possible to remove from a wide range of cesium contaminated (20-400 mg/L) wastewater [30].

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