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Efficient nitrate removal by Ca-treated activated carbon derived from agricultural residues

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ABSTRACT

Various agricultural residues such as bamboo chips, bagasse bottom ashes, corncobs and macadamia nutshells were used to prepare activated carbon by steam activation. These materials were further treated by $Ca(OH)_2$ and HCl solution, and the sample originated from bamboo was the best for nitrate removal from water. In addition, the bamboo activated carbon was treated with high concentrations of $CaCl_2$ and HCl solution (BC-CL-A), showing a greater adsorption amount for nitrate removal. BC-CL-A exhibited a nitrate adsorption capacity (0.45 mmol g^{-1}) approximately twice as much as that of the untreated sample. The nitrate adsorbed on BC-CL-A was easily desorbed from the surface by KCl solution due to ion exchange between NO_3^- and Cl^-. Regeneration test for BC-CL-A by KCl solution was also examined. After three cycles of regeneration, the adsorbed nitrate could be removed by 88.6%, implying that some nitrates were irreversibly adsorbed on BC-CL-A.

Keywords: Nitrate; Adsorption; Activated carbon; Ion exchange

1. Introduction

In recent years, various water resources have been severely polluted by nitrogen containing compounds, such as nitrate/nitrite and ammonium, which may cause serious environmental problems including eutrophication [1]. Especially nitrate can cause severe infection diseases, such as cyanosis of mucous membrane and cancer of the alimentary canal [2]. Excess nitrate in drinking water may lead to methemoglobinemia for infants as a result of the conversion of hemoglobin into methemoglobin, which acts as an inhibitor for the oxygen transfer system [3]. Therefore, investigating the effective method of nitrate removal is desired to preserve water quality. Several methods such as biological de-nitrification [4], reverse osmosis [5], adsorption [6], and ion exchange [7] have been attempted to remove nitrate so far. Among these methods, adsorption is an effective method due to its simplicity and ease of operation [8].

Nowadays, many types of agricultural residues are disposed every year, and effective utilization of these is expected. They are relatively cheap and can be utilized as renewable resource of activated carbon (AC) [9], and also as ion exchangers [10]. AC can be prepared inexpensively from various agricultural residues without any special facilities, so it has been used in many countries. Generally, AC is a typical and useful adsorbent for organic compounds because of its large surface area and pore volume. However,

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it has poor performance for removal of ionic compounds such as heavy metal ion, phosphate ion, and nitrate ions due to its hydrophobic surface property [11].

Surface acidic functionalities of carboxylic groups on AC are known to play an important role as adsorption sites for heavy metal such as cadmium and lead cations via ion exchange onto the surface of AC [12]. On the other hand, improvement of adsorption ability of nitrate anion has been reported by using wood waste through Ca-impregnation, thermal decomposition and acid treatment by HCl(aq.) [13]. Adsorption of nitrate can take place through ion exchange between NO_3^- and Cl^- on AC surface, and in contrast, adsorbed nitrate can be desorbed from AC surface easily in the presence of large amounts of Cl^- ions.

In this study, various ACs were prepared by steam activation from several agricultural residues (bamboo chip [BC], bagasse bottom ash [BBA], corncob (CC) and macadamia nutshell [MC]). Each AC was soaked in $Ca(OH)_2$ and HCl solution to improve nitrate adsorption capacity. $CaCl_2$ solution was also used for BC AC in order to compare with $Ca(OH)_2$ solution. We conducted Ca modification for AC without thermal decomposition in order to confirm whether thermal treatment is necessary or not for the improvement of nitrate adsorption capacity. The pore structure and surface chemistry were inspected for each sample. Furthermore, elution tests as well as adsorption experiments were conducted. The results were compared with those of commercial AC.

2. Experimental

2.1. The material

BCs, BBAs, CCs and MCs were used as precursors for the preparation of ACs. Commercially available coconut shells-based AC (CAC) (C. Gigantic Carbon Co.,Ltd.,NakornRatcahsima, Thailand) was used to compare various properties with the prepared samples. In the carbonization treatment, the dried samples were put into a crucible and carbonized at several temperatures ranging from 300°C to 800°C as shown in Table 1, under a nitrogen (N_2) gas flow at 200 $cm^3\ min^{-1}$ for 1 h, at a heating rate of 20°C min^{-1}. The proximate analysis for each char was determined on a dry basis by a thermogravimetry analyzer (TGA) (Pyris 1 TGA, PerkinElmer, Waltham, Massachusetts). Moisture, volatile matter and ash content for each sample were calculated using standard methods of the American Society for Testing and Materials (1996) through ASTM D 2867-96, ASTM D 5832-96 and ASTM D 2866-96, respectively [14]. In the activation step, each sample was placed into a muffle furnace, and the tube was heated under a flow of N_2 gas. When the furnace temperature reached the corresponding carbonization temperature, steam generated from a heating pot with a constant flow rate of 8 g min^{-1} under the pressure of 1.0 kg cm^{-2} was introduced. The sample was heated to 800°C and maintained for 1 h under the steam atmosphere. The resulting carbons were cooled to room temperature under N_2 gas atmosphere to remove moisture resulted from steam.

2.2. Carbon modification

Approximately 2 g of each AC (BC, BBA, CC, MC and CAC) was crushed into a particle size of 100 to 200 μm and impregnated with 100 mL of 20 mM $Ca(OH)_2$ solution, agitating at 100 rpm for 24 h at 30°C. The impregnated samples were washed with distilled water and dried at 60°C overnight. After that, the samples were added into 100 mL of 4 M HCl solution and then treated with the same procedure described above for agitation, washing and drying. AC treated with only HCl solution was also prepared for comparison. Each sample was labeled as follows; "BC", for instance, BC-A: when treated with HCl acidic solution, and BC-OH-A: when treated with $Ca(OH)_2$ followed by HCl acidic solution. Since it has been reported that $CaCl_2$ is easier to dissolve in water than $Ca(OH)_2$ and can be an effective reagent to improve nitrate removal [15], approximately 20 mM $CaCl_2$ and 5 M $CaCl_2$ solution were used to modify BC in accordance with a similar procedure to the HCl acid treatment, and these samples were designated as BC-cl-A and BC-CL-A, respectively.

2.3. Measurement of pore structure

The porous properties of the prepared ACs were measured by the adsorption-desorption isotherms of nitrogen gas at –196°C with a surface area and pore size analyzer (Beckman Coulter, SA-3100, Brea, California). The Brunauer–Emmett–Teller (BET) equation was applied to estimate the specific surface area (S_{BET}) [16]. The total pore volume (V_{total}) was determined from N_2 adsorption capacity at a relative pressure of 0.99. The subtracting pore effect method using α_s-plot was applied to obtain the micropore volume (V_{micro}) [17].

2.4. The pH of the point of zero charge (pH_{pzc})

The pH of the point of zero charge (pH_{pzc}) indicates no electrical charge on the surface of AC. 50 milligram of the sample was added into a 25 mL solution, in which the initial pH (pH_0) was adjusted from 1 to 12 with 0.1 M HCl or NaOH, and agitated at 100 rpm for 24 h at 30°C. After that, the equilibrium pH (pH_e) of each solution was measured to determine the pH_{pzc} using the pH drift method [18]. The pH_{pzc} is the point where the curve of pH_0 vs. pH_e intersects with the line of $pH_0 = pH_e$. As shown in Fig. 1, for example, pH_{pzc} for BC can

Table 1
Proximate analysis of chars from various agricultural residues

Sample	Carbonization temp. [˚C]	Volatile matter [wt%]	Fixed carbon [wt%]	Ash [wt%]
Bamboo chip	800	14.1	71.4	14.5
Baggase bottom ash	300	18.1	57.5	24.4
Corncob	500	20.7	76.0	3.3
Macadamia nut-shell	500	17.4	81.8	0.8

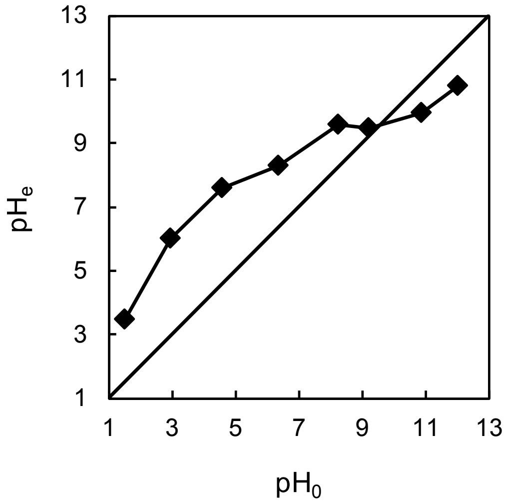

Fig. 1. The pH of the point of zero charge (pH_{pzc}) of bamboo chip activated carbon (BC), determined by the pH drift method.

be determined to be 9.6. The solution pH was measured using a pH meter (Delta 340, Mettler Toledo, Switzerland).

2.5. Fourier Transform Infrared (FT-IR) analysis

Fourier Transform Infrared (FT-IR) spectra of the carbon samples were obtained by using FT-IR spectroscopy (TENSOR 27, Bruker, USA) in the range of wave numbers from 4,000 to 600 cm^{-1}. The samples were mixed with KBr at a ratio of 1 g sample: 750 g KBr, and the mixture pressed into a 1-mm pellet. Then, the samples were analyzed with the spectral resolution of 1 cm^{-1}.

2.6. X-ray fluorescence (XRF) analysis

Wavelength Dispersive X-ray Fluorescence (WD-XRF) Spectrometer (S4-Pioneer: Bruker AXS, Germany) was used to determine the elemental composition of each sample. The WD-XRF was equipped with an end window Rh-target X-ray tube with a maximum output of 4 kW and eight diffracting crystals of various d-spacings. 2 g of the samples were put into a sample cup underlaid with 4-micron prolene foil on the bottom of the cup. The cups were then introduced into the sample slots of the WD-XRF and analyzed to determine the elemental composition of the samples.

2.7. Adsorption experiments

The adsorption study for nitrate ions was conducted in batch experiments. Approximately 50 mg of each sample was added into 25 mL of $NaNO_3$ solution in a 125 mL Erlenmeyer flask, and the mixture was stirred at 100 rpm for 24 h at 30°C. The initial concentration of nitrate ion ranged from 10 to 300 mg L^{-1}. No pH adjustment for nitrate solution was carried out for all adsorption experiments. After the adsorption experiment, the solution was removed by decantation, and nitrate ion concentration of the sample was determined by UV-visible spectrophotometer (DR/2500 Spectrophotometer, Hach, USA) based on cadmium reduction method [19]. A wavelength of 500 nm was selected because the peak absorbance of nitrate ion could be observed in this UV region. Since utilizing standard deviation is recommended with three repetitions, all adsorption experiments were conducted in triplicate, and the result was represented as the mean value (n = 3). The experimental data were analyzed using the Langmuir and Freundlich models [20]. The Langmuir isotherm can be expressed by:

$$\frac{C_e}{Q_e}=\frac{1}{X_m}C_e+\frac{1}{X_mK_e} \tag{1}$$

where Q_e (mmol g^{-1}) is the adsorptive amount of nitrate ion at equilibrium; C_e (mmol L^{-1}) is the equilibrium concentration of nitrate ion in the solution; and X_m (mmol g^{-1}) and K_e (L $mmol^{-1}$) are the maximum adsorption capacity and the adsorption affinity, respectively. The Freundlich isotherm is given by:

$$\log Q_e=\log K_F+\frac{1}{n}\log C_e \tag{2}$$

where K_F [(mmol g^{-1})(L $mmol^{-1})^{1/n}$] and n are the Freundlich constants and indicate the adsorption intensity.

2.8. Elution test

Elution tests were performed to investigate the adsorption mechanism of nitrate and the possibility of regeneration for the sample. An initial nitrate concentration of 100 mg L^{-1} was used, and after the adsorption was reached at equilibrium, nitrate-adsorbed samples were collected by filtration. The samples were transferred to different 125 mL Erlenmeyer flasks, and 25 mL of 0.1 M NaOH or 1 M KCl solution was added into the flasks. The flasks were agitated at 100 rpm for 24 h at 30°C, and the concentration of the eluted nitrate was measured in the same manner as mentioned above. All elution experiments were conducted in triplicate, and the result was represented as the mean value (n = 3).

3. Results and discussion

3.1. Sample properties

The proximate analysis of chars originated from various agricultural residues is given in Table 1. There was not much difference in the volatile matter contents among the samples. Since bagasse bottom ash had low fixed carbon content and high ash content, these properties were not suitable for the production of AC. On the other hand, MC was supposed to be good precursor for AC due to higher fixed carbon and lower amount of ash.

Table 2 indicates specific surface area, pore volume and pH_{pzc} of each prepared AC. To investigate maximum adsorption capacity of nitrate for each AC, the optimum activation temperature was selected to obtain the maximum surface area [21]. BC had the highest S_{BET} and V_{total} of 1,120 m^2 g^{-1} and 0.79 cm^3 g^{-1}, respectively, though CAC had higher V_{micro} value than that of BC. The result indicated that BC itself had high potential to develop larger pore structure. BBA showed the lowest S_{BET} and V_{micro} of 588 m^2 g^{-1} and 0.12 cm^3 g^{-1}, respectively, implying that high ash content of BBA disturbed

Table 2
Porous and surface properties of each activated carbon

Sample	Steam activation temp. (°C)	S_{BET} ($m^2 g^{-1}$)	V_{total} ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	pH_{pzc}
Bamboo chip activated carbon (BC)					
BC	800	1,120	0.79	0.40	9.6
BC-A	800	1,090	0.77	0.39	2.5
BC-OH-A	800	1,080	0.77	0.39	2.2
Bagasse bottom ash activated carbon (BBA)					
BBA	800	588	0.53	0.12	9.5
BBA-A	800	570	0.52	0.12	2.7
BBA-OH-A	800	522	0.49	0.10	2.6
Corncob activated carbon (CC)					
CC	800	711	0.39	0.31	9.1
CC-A	800	654	0.37	0.30	1.7
CC-OH-A	800	609	0.35	0.29	1.9
Macadamia nutshell activated carbon (MC)					
MC	800	942	0.52	0.29	9.1
MC-A	800	940	0.52	0.28	1.9
MC-OH-A	800	901	0.50	0.27	1.9
Commercial activated carbon (CAC)					
CAC	–	1,100	0.49	0.43	9.0
CAC-A	–	1,070	0.48	0.42	2.0
CAC-OH-A	–	1,060	0.48	0.42	2.0

improvement of porous properties. By $Ca(OH)_2$ and HCl acid treatment, the surface area slightly decreased and the pH_{pzc} was drastically lowered for all samples due to the presence of H^+ adsorbed through HCl acid treatment.

3.2. Nitrate adsorption

Fig. 2 shows results of the nitrate adsorption experiment using each prepared AC. There was no clear correlation between the porous property and nitrate adsorption capacity of each untreated sample, and CAC showed the lowest nitrate adsorption capacity among the other samples. This is due to the hydrophobic surface of CAC, which is not favorable to attract ionic materials. The pH values in the equilibrium solution for untreated and HCl treated samples were around 7–8 and 3–4, respectively. The adsorption of nitrate increased under acidic condition, which would attribute to an electrostatic attraction between negatively charged nitrate ion and positively charged carbon surface [22]. The presence of H^+ on the carbon surface could enhance the nitrate adsorption. BC-A and CC-A showed higher nitrate adsorption capacity than corresponding BC and CC, suggesting that a large amount of H^+ was easily accommodated onto the high surface area of BC and CAC (Table 2). In addition, the nitrate adsorption capacity increased for BC-OH-A and CC-OH-A, indicating that Ca^{2+} introduced to the carbon surface could easily adsorb Cl^-. The adsorbed Cl^- by the HCl treatment could cause anion exchange with nitrate ion. However, no or only slight improvement of nitrate adsorption was observed for BBA-OH-A, MC-OH-A and CAC-OH-A. This might be caused by some poor interaction of Ca^{2+} and the carbon surface. Since BC-OH-A was the best adsorbent for nitrate removal, BC was chosen to examine the adsorption mechanism of nitrate adsorption. The results of nitrate adsorption by BC-OH-A, BC-cl-A and BC-CL-A are provided in Fig. 3. BC-OH-A and BC-cl-A reached 0.35 mmol g^{-1} of nitrate adsorption, whereas BC-CL-A showed approximately 0.40 mmol g^{-1}, indicating that the concentration of Ca^{2+} slightly contributed to nitrate adsorption.

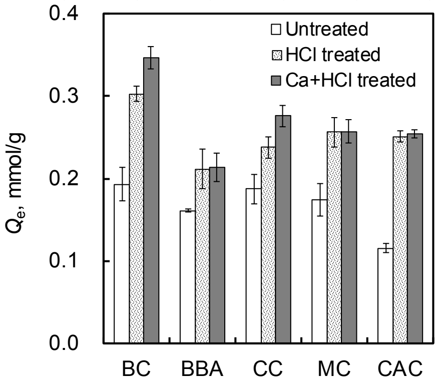

Fig. 2. Nitrate adsorption capacity of bamboo chip activated carbon (BC), bagasse bottom ash activated carbon (BBA), corncob activated carbon (CC), macadamia nut shell activated carbon (MC) and commercial activated carbon (CAC) under HCl and $Ca(OH)_2$ + HCl treatment (Initial nitrate concentration = 100 mg/L, pH 7 at 30°C). The error bars represent the standard deviation of three replicates.

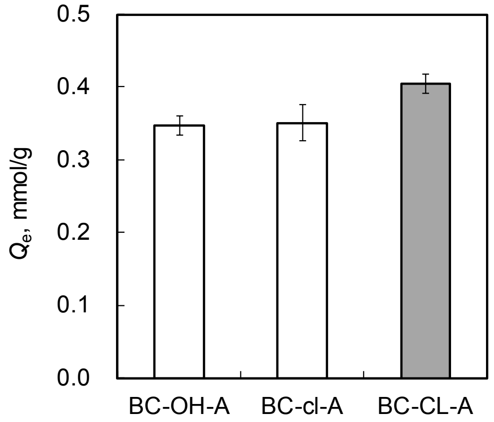

Fig. 3. Comparison of nitrate adsorption capacity of bamboo chip activated carbon treated with 20 mM $Ca(OH)_2$ + HCl (BC-OH-A), bamboo chip activated carbon treated with 20 mM $CaCl_2$ + HCl (BC-cl-a) and bamboo chip activated carbon treated with 5 M $CaCl_2$ + HCl (BC-CL-A). The error bars represent the standard deviation of three replicates.

3.3. FT-IR spectra

This experiment was conducted to investigate the various functional groups onto the carbon surface. Fig. 4 shows FT-IR spectra of BC, BC-OH-A and BC-CL-A. The peak at 3,600–3,200 cm^{-1} was assigned to O–H stretching vibration [23]. The peaks at 2,920, 2,850 and 1,400 cm^{-1} were related to the aliphatic groups [24]. Although the band around 1,600 cm^{-1} was often found in various carbon materials [25], the origin is still not clearly identified. The bands around 1,600 cm^{-1} would be attributed to an aromatic carbon or carbonyls according to various studies [26–28]. The sharp peak at 1,380 cm^{-1} was probably related to N=O stretching [29]. The peak at 1,020 cm^{-1} was attributed to C–O stretching vibration of ether, and the peak at 1,100 cm^{-1} that appeared by Ca and HCl acid treatments suggests the presence of alcoholic and phenolic groups formed by the reaction between HCl and carbon surface functional groups [23].

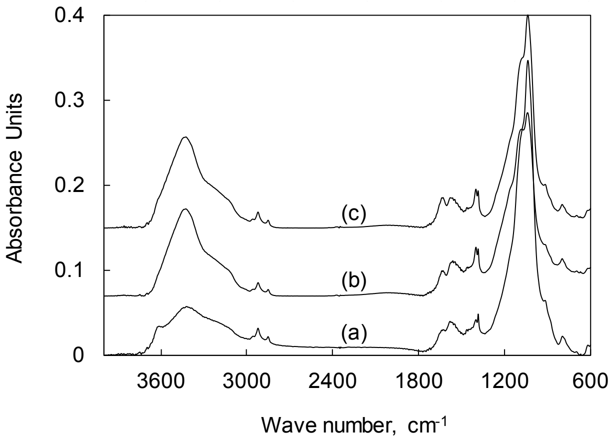

Fig. 4. FT-IR spectra of (a) bamboo chip activated carbon (BC), (b) bamboo chip activated carbon treated with 20 mM $Ca(OH)_2$ + HCl (BC-OH-A) and (c) bamboo chip activated carbon treated with 5 M $CaCl_2$ + HCl (BC-CL-A).

3.4. XRF

The result of XRF for BC, BC-A and BC-CL-A is summarized in Table 3. The Cl contents in BC, BC-A and BC-CL-A were 2.34, 8.96 and 18.3 wt%, respectively, and the Ca content in BC-CL-A was about 36 times higher than BC. Ca and Cl were easily introduced to the carbon surface by the modification. Particularly Cl content in BC-CL-A was about twice higher than that of BC-A implying that Cl$^-$ was readily held on to the carbon surface through Ca^{2+} ions. Therefore, nitrate adsorption capacity was probably improved in BC-CL-A since anion exchange between NO_3^- in solution and the large amount of Cl$^-$ on adsorbent could easily occur.

3.5. Adsorption isotherm

Adsorption isotherms of CAC, BC and BC-CL-A at the initial nitrate concentration from 10 to 300 mg L^{-1} are represented in Fig. 5, and the parameters obtained from Langmuir and Freundlich equations are listed in Table 4. The

Table 3
Elemental composition of bamboo chip activated carbon (BC), bamboo chip activated carbon treated with HCl (BC-A) and bamboo chip activated carbon treated with 5M $CaCl_2$ + HCl (BC-CL-A)

Sample	Ca (wt%)	C1 (wt%)	Si (wt%)	Others (C, H, N, etc.)
BC	0.09	2.34	13.5	84.1
BC-A	0.07	8.96	10.9	80.1
BC-CL-A	3.64	18.3	6.78	71.3

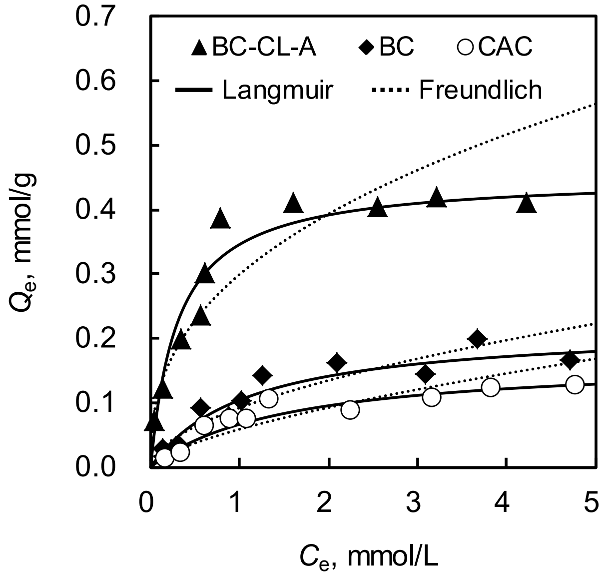

Fig. 5. Adsorption isotherms of nitrate on commercial activated carbon (CAC), bamboo chip activated carbon (BC) and bamboo chip activated carbon treated with 5 M $CaCl_2$ + HCl (BC-CL-A) at 30°C.

Table 4
Langmuir and Freundlich parameters of nitrate adsorption on commercial activated carbon (CAC), bamboo chip activated carbon (BC) and bamboo chip activated carbon treated with 5M $CaCl_2$ + HCl (BC-CL-A)

Sample	Langmuir parameter			Freundlich parameter		
	X_m (mmol g^{-1})	K_e (L $mmol^{-1}$)	R^2	K_F [(mmol g^{-1})(L $mmol^{-1}$)$^{1/n}$]	n	R^2
CAC	0.17	0.65	0.92	0.06	1.53	0.86
BC	0.22	0.91	0.92	0.09	1.82	0.88
BC-CL-A	0.45	3.28	0.99	0.30	2.54	0.91

Table 5
Maximum adsorption capacity of nitrate on various materials

Starting material	Activation agent	Thermal treatment temp. (°C)	X_m (mmol g^{-1})	Reference
Bamboo chip activated carbon	$CaCl_2$ + HCl	–	0.45	This work
Hinoki chip	$Ca(OH)_2$ + HCl	700	0.92	[13]
Coffee ground	$CaCl_2$ + HCl	600	0.37	[15]
Anionic exchange resin (AER)	–	–	0.89	[13]

adsorption isotherms of CAC, BC and BC-CL-A were fitted well to the Langmuir model rather than the Freundlich model based on the value of R^2, suggesting that the nitrate adsorption would take place on a homogeneous surface in a single layer. The X_m value of BC-CL-A was 0.45 mmol g^{-1}, and it was a 2.0–2.5 times higher value than those of CAC and BC. Moreover, BC-CL-A had a 3–5 times higher K_e value than the other samples, implying that nitrate adsorbed on the carbon surface by ion exchange between NO_3^- in solution and Cl^- on adsorbent was relatively dominant compared with other adsorption forms.

Table 5 lists the comparison of maximum adsorption capacity of nitrate on various materials. The sample prepared from hinoki chip showed the highest nitrate adsorption capacity of 0.92 mmol g^{-1} [13]. This value was even higher than that of anionic exchange resin; therefore, $Ca(OH)_2$ + HCl and thermal treatment for hinoki chip could be a significantly effective method for improvement of nitrate adsorption. On the other hand, the sample prepared from coffee ground represented lower nitrate adsorption capacity than that of this work's sample [15]. Thereby, $CaCl_2$ and HCl acid treatment without thermal decomposition could also be effective to nitrate removal. The thermal treatment of each material soaked in Ca solution could contribute to make the strong bond, which called calcite, between Ca and the surface of the carbon [13]. This calcite remained after the acid treatment and enhanced the nitrate adsorption capacity via anion exchange. In this work, the nitrate adsorption capacity increased without thermal treatment; therefore, the calcite was produced on the carbon surface and influenced the adsorption process.

3.6. Regeneration study

Fig. 6 shows elution as a percentage of nitrate-loaded CAC, BC and BC-CL-A using 0.1 M NaOH or 1 M KCl solution. The nitrate elution of CAC and BC was approximately 96%–97% by using NaOH solution, whereas BC-CL-A had lower elution percentage of 81% suggesting that some nitrates were strongly adsorbed onto the BC-CL-A surface. Therefore, some strong interactions such as chemisorption might be involved in the nitrate adsorption for BC-CL-A. Contrarily, nitrate adsorbed on BC-CL-A could be easily removed by using KCl solution as eluent. Generally, nitrate desorption is pronounced at a basic pH range since a large amount of OH^- inhibits nitrate adsorption [30]. The pH value of KCl solution was around 7, thereby the elution of CAC and BC was reduced. KCl solution has often been used to desorb an adsorbate because the considerable amount of Cl^-

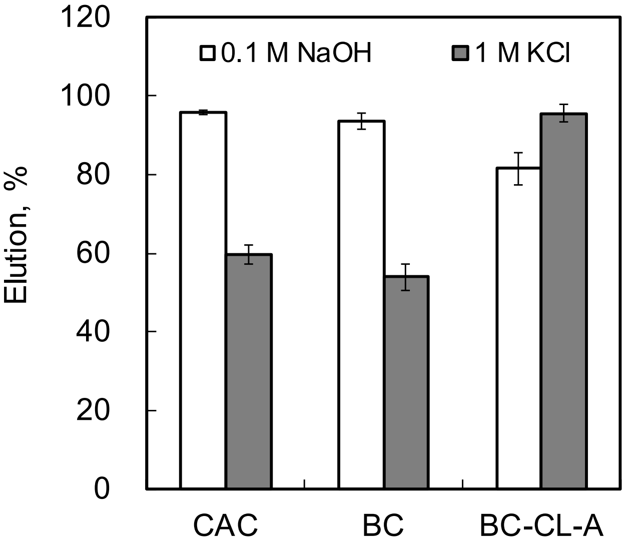

Fig. 6. Percentage of nitrate elution from nitrate adsorbed on commercial activated carbon (CAC), bamboo chip activated carbon (BC) and bamboo chip activated carbon treated with 5 M $CaCl_2$ + HCl (BC-CL-A) using 0.1 M NaOH and 1 M KCl solution. The error bars represent the standard deviation of three replicates.

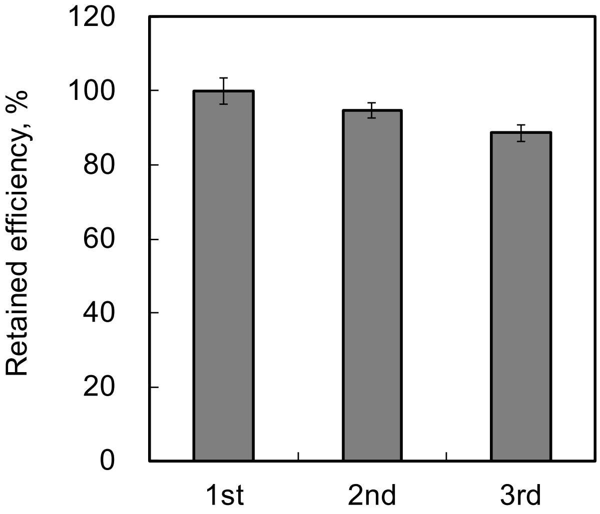

Fig. 7. Recycle of nitrate adsorption by bamboo chip activated carbon treated with 5 M $CaCl_2$ + HCl (BC-CL-A) using 1 M KCl as an eluent. The error bars represent the standard deviation of three replicates.

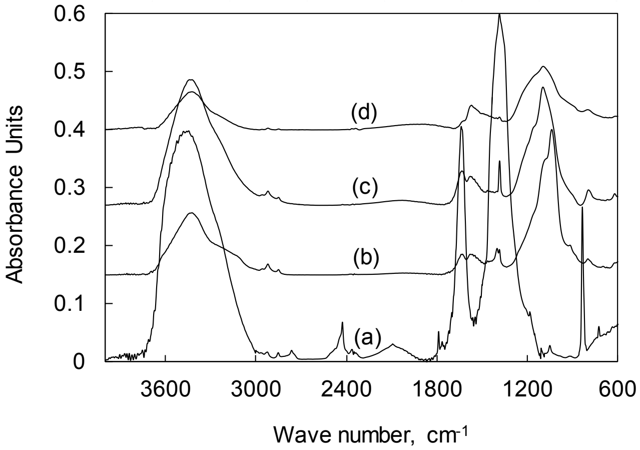

Fig. 8. FT-IR results of (a) $NaNO_3$, (b) bamboo chip activated carbon treated with 5 M $CaCl_2$ + HCl (BC-CL-A), (c) nitrate-loaded BC-CL-A and (d) nitrate-desorbed BC-CL-A.

in KCl can cause ion exchange between Cl^- and the adsorbate as NO_3^- [31]. The high elution of BC-CL-A could be suggested to be caused by the ion exchange by KCl solution.

Reuse of the adsorbent was studied using nitrate-adsorbed BC-CL-A. KCl solution was employed to remove nitrate from BC-CL-A so that the anionic nitrate adsorbed on BC-CL-A could be exchanged by the presence of an abundant amount of Cl^- ions in the solution. The recovered material was washed with distilled water and dried at 60°C. Consecutive adsorption/desorption cycles were performed to study the feasibility of regeneration of BC-CL-A in limited conditions. Fig. 7 shows the adsorption performance of BC-CL-A regenerated using KCl. After the third regeneration, the nitrate adsorption capacity of BC-CL-A was retained at 88.6% suggesting that a part of nitrate was adsorbed strongly onto BC-CL-A.

3.7. FT-IR analysis for BC-CL-A before and after elution

FT-IR spectra of $NaNO_3$, BC-CL-A, nitrate-loaded BC-CL-A and nitrate-desorbed BC-CL-A by KCl are shown in Fig. 8. $NaNO_3$ had a sharp and large peak located at 1,380 cm^{-1} which was attributed to N=O stretching [29], while for the adsorbent, the height of peaks at 1,380 cm^{-1} was enhanced with the adsorption experiments. This result is caused by the nitrate adsorption on the BC-CL-A surface. In addition, the peak at 1,380 cm^{-1} obviously became weaker after the elution with KCl solution due to desorption of nitrate from BC-CL-A.

4. Conclusion

Among the various agricultural materials, the AC originated from BC provided the highest nitrate adsorption capacity by $Ca(OH)_2$ modification. $CaCl_2$ treatment in high concentration was effective to enhance the adsorption capacity of nitrate for bamboo AC. The unique functional groups could not be identified in Ca- and HCl-treated samples; however, Ca and Cl were confirmed to be introduced to the carbon surface from XRF analysis. Based on the results of adsorption equilibrium isotherms of nitrate, the adsorption processes were well fitted to Langmuir equation. The basic solution was effective as eluent in the elution experiments and a high-concentration KCl solution could also easily remove nitrate via ion exchange process to regenerate the adsorbents.

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