Investigating the effective carbon material for thermal chemical vapor deposition using aniline to enhance As(V) adsorption capacity of activated carbon

Pyunghwa Yoo¹ · Yoshimasa Amano^{2,3} · Motoi Machida^{2,3}

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Abstract

To enhance the arsenic(V) adsorption capacity in the wide pH range, thermal chemical vapor deposition (tCVD) using aniline was conducted on various raw materials to prepare nitrogen-doped activated carbon samples. Phenol resin, polyacrylonitrile-based carbon fiber, cellulose-based activated carbon fiber, petroleum-derived beads-shaped activated carbon, and plant-based activated carbon powder were used as activated carbon precursors. We conducted the consecutive treatment (CVD) of steam activation as a pretreatment (8ST30), aniline tCVD (8ANL10), steam activation (8ST50), and heat treatment (9.5HT30). Steam activation was performed to improve tCVD efficiency and specific surface area. The annealing process at 950 °C was conducted to form quaternary nitrogen (N-Q) and reduce oxygen-containing acidic functional groups on the surface. The best result was obtained when we used cellulose-based activated carbon fiber as a precursor (KF-CVD). KF-CVD showed 0.172 mmol/g of the arsenic adsorption capacity, and it was at least 46% larger than that of all prepared samples. KF-CVD also indicated the highest adsorption capacity at any pH range. We assessed porous properties, elemental composition, nitrogen configuration by X-ray photoelectron spectroscopy, the number of surface functional groups by Boehm titration, and pH_{pzc} of the prepared samples. Based on these surface characteristic studies; the increased specific surface area and the highest N-Q content of KF-CVD would enhance the arsenic adsorption in all pH ranges.

Keywords Activated carbon · Boehm titration · Adsorption · Arsenate · Chemical vapor deposition · Quaternary nitrogen

1 Introduction

Arsenic contamination is reported worldwide, e.g., in India [1], China [2], and Canada [3]. Arsenic, which is a toxic metalloid, can be found in natural sulfidic minerals or sediments. These natural arsenic compounds are generally released into water by global geochemical activities such as volcanic activities and weathering reactions. Besides, human activities such as using pesticides and

herbicides, mining, smelting, digging wells also release anthropogenic arsenic compounds into nature [4–6]. The main inorganic species of released arsenic in nature are the inorganic form. Trivalent arsenic, which is the main species in anaerobic condition, was reported to be greater toxicity than pentavalent arsenic [7]. Oral ingestion of pentavalent arsenic also reduced into trivalent arsenic in the human body, causing various skin diseases including cancer [1–8]. Not only drinking contaminated water but also

✉ Pyunghwa Yoo, ypha2000@naver.com; Yoshimasa Amano, amanoy@faculty.chiba-u.jp; Motoi Machida, machida@faculty.chiba-u.jp

¹Graduate School of Science and Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan. ²Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan. ³Safety and Health Organization, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan.

consuming crops is the major arsenic source to humans [9]. Due to these health risks, the World Health Organization (WHO) has determined the drinking water quality to be 0.01 mg-As/L or less [10]. Accordingly, the removal of excessive arsenic from water has been required.

To remove excessive arsenic from water, oxidation [11], flocculation [12], filtration [13], and adsorption methods [14–16] have been reported. Among these methods, adsorption needs only a simple operation process. Activated alumina [17], iron-coated adsorbents [18], ion exchange resin [19], and activated carbon [16, 20] can be utilized as an adsorbent. Activated carbon is usually prepared from waste such as garlic stem [16], millet stalk and cashew shell [20], and the production costs would be cheaper than other adsorbents. In addition to the fact that carbon materials have stronger resistance against heat and acid than other polymeric ion exchangers, activated carbon has more flexible applications than other adsorbents.

In our previous studies, heating and nitrogen-doping treatments increased the anion adsorption capacity of activated carbons. Heating activated carbon at 950 °C for enhancing the π -electrons on the graphene layer by decomposition of oxygen-containing acidic functional groups was conducted [21]. Ota et al. [21] reported that the π -electrons on the graphene layer can attract some protons resulting in a slight increase of adsorption site and decomposition of oxygen-containing acidic functional groups by annealing process would enhance the π -electrons because these functional groups are known as electron-withdrawing groups. We also demonstrated that the heat treatment gave sample hardness against steam activation; therefore, we must conduct the annealing process at the last step because steam activation could not be conducted properly after the annealing [22, 23]. Moreover, forming quaternary nitrogen from the other surface nitrogen species by heat treatment was conducted [24, 25]. From these studies, we assumed that introducing nitrogen on the carbon material would enhance the N-Q content on the heat-treated activated carbon surface. Therefore, we used the thermal chemical vapor deposition (tCVD) process to prepare nitrogen-doped samples. Acetonitrile [23, 26], melamine [27], and aniline [22] showed a good nitrogen supplier. According to our previous study [22], the increased N-Q due to the introduced nitrogen and quaternization by annealing process enhanced anion adsorption capacity. However, steam activation was essential before and after the tCVD process. This is because a high specific surface area is required to expand the contact area between nitrogen-containing compound gas and precursors surface. Furthermore, porous surface was sealed due to the newly formed surface structure by the tCVD treatment. For the above reasons, previous studies showed that continuous treatment method of introducing

30 mL of distilled water at 800 °C (8ST30), 10 mL of aniline at 800 °C (8ANL10), 50 mL of distilled water at 800 °C (8ST50), and at last heating for 30 min at 950 °C (9.5HT30) was the best method. On the other hand, we did not discuss the relationship between the physicochemical surface properties of the various precursors and the efficiency of the 8ST30-8ANL10-8ST50-9.5HT30 process in previous study [22]. Therefore, this study compared the adsorption amount and surface characteristics of prepared samples to decide which was suitable as a raw material for arsenic adsorption. The phenol resin, which was used in our previous study [22], had nearly zero in nitrogen content. In this study, we prepared samples from nitrogen-rich polyacrylonitrile (PAN)-based carbon fibers to investigate the effect of the nitrogen content as starting carbon material. Besides, to confirm the relationship between the specific surface area of the raw material and the efficiency of the optimized treatment (8ST30-8ANL10-8ST50-9.5HT30), a sample was prepared from cellulose-based activated carbon fibers. Additionally, beads-shaped activated carbons derived from petroleum and plant-based activated carbon powders were used as precursors for examining the effect of original surface properties of the activated carbons on the adsorption capacity of As(V).

2 Materials and methods

2.1 Reagents

All the reagents used in this study were analytical grade and used without further purification. All used precursors and their manufacturers are listed in Table 1. All precursors were used after drying at 110 °C for at least 1 h to remove water from the surface. For comparison, we used anion exchange resin (HP555). In case of the HP555, we dried the adsorbent at 40 °C for 12 h before use.

2.2 Adsorbent preparation

All treatments were performed in a tubular reactor consecutively. The quartz tube was used as a reactor, and it was 28 mm outer diameter $\times$ 24 mm inner diameter $\times$ 0.50 m length in size. All experimental methods were performed under a helium flow, and the initial amount of the precursor was 3 g. Under these experimental conditions, we conducted the combination of heat treatment, steam activation, and thermal chemical vapor deposition (tCVD). For the heat treatment, samples were heated at 950 °C for 30 min. The main purpose of heat treatment is to remove oxygen from the surface of ACs and quaternization of surficial nitrogen. The samples treated in these processes were named as

Table 1 Precursors and original manufacturer

Precursor name	Abbreviation of precursor	Manufacturer
Phenol resin (Kynol Fiber KF-0270)	PhR	Gun Ei Chemical Industry Co., Ltd.
Air-stabilized polyacrylonitrile (PAN)-based fiber (PYROMEX)	Pyromex	Teijin Ltd.
Activated carbon fiber made from cellulosic fibers (KF1500LDA)	KF	Toyobo Co. Ltd.
Highly spherical activated carbon made from petroleum pitch (BAC)	BAC	KUREHA Corp.
Plant-based activated carbon powder (NORIT® CGP SUPER)	CGP	Cabot Corp.

Nippon Dionex KK), and arsenate adsorption capacity at the equilibrium state was calculated by the following equation:

$$Q_e = \frac{(C_0 - C_e)v}{w}, \quad (1)$$

where C_0 and C_e depict the initial and the equilibrium arsenate concentrations (mmol/L), respectively. v represents solution volume (mL) and w indicates the adsorbent weight (mg).

The obtained experimental adsorption data were fitted to the Langmuir and Freundlich isotherm models [30]. Langmuir isotherm model which was used in this study is represented as the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L}, \quad (2)$$

where C_e describes the arsenate concentration at equilibrium state. K_L (L/mmol) is referred to as the Langmuir isotherm constant. Q_e and Q_m (mmol/L) are the adsorption capacity at the equilibrium and maximum adsorption capacity, respectively. Freundlich isotherm model can be written as the following equation:

$$Q_e = K_F C_e^{1/n}, \quad (3)$$

where K_F [(mmol/g)(L/mmol)^{1/n}] and n represent the Freundlich isotherm constant. K_F [(mmol/g)(L/mmol)^{1/n}] is related to adsorption capacity and $1/n$ related to the heterogeneity of the surface. Because the adsorption capacity reached equilibrium adsorption states around 100 mg-As(V)/L, we used 100 mg-As(V)/L solution as initial concentration for other adsorption tests.

2.4 Adsorbent properties

Surface porosity of the prepared ACs was assessed by BET measurement using N₂ adsorption/desorption isotherms at −196 °C (BELSORP-mini II, MicrotracBEL). Samples were outgassed at 300 °C for 1 h before conducting the BET measurement. The specific surface area (S_{BET} , m²/g) and average pore diameter (D_{avg} , nm) of the samples were obtained by using BET method. The total pore volume (V_{total} , cm³/g) was also quantified from the maximum nitrogen adsorption capacity at a relative pressure of 0.990. The micropore volume (V_{micro} , cm³/g) was calculated by t -plot method [31]. The mesopore volume (V_{meso} , cm³/g) was calculated by the difference between V_{total} and V_{micro} .

CHN elemental analysis was conducted to find out the elemental composition of the prepared samples (PE2400II, Perkin Elmer). CVD-treated samples and activated carbons

which were used as raw materials were incinerated for 1 h at 815 °C for the measurement of ash content.

Surface nitrogen species of the prepared samples were evaluated by X-ray photoelectron spectroscopy (JPS-9030, JEOL). Surface nitrogen was assumed to be pyridinic nitrogen (N-6, 398.7 ± 0.3 eV), pyrrolic nitrogen (N-5, 400.4 ± 0.3 eV), quaternary nitrogen (N-Q, 401.1 ± 0.3 eV) and pyridine-N-oxide (N-X, 402–404 eV) which were reported by Pels et al. [25].

Boehm titration method [32] was used to appraise the amount of surface functional groups on the prepared activated carbon samples. Solutions of 0.05 mol/L Na₂CO₃, 0.1 mol/L NaHCO₃, 0.1 mol/L NaOH and 0.1 mol/L HCl were prepared and added in a 100-mL Erlenmeyer flask with the prepared samples. The flasks were agitated for 4 days at room temperature. After the shaking process, 5 mL of each solution was sampled and titrated with 0.05 mol/L HCl. In the case of the 0.1 mol/L HCl, 10 mL of 0.1 mol/L NaOH was added to perform back titration.

The pH_{pzc} of the prepared samples was evaluated by pH drift method [33]. Using distilled water, hydrochloric acid, and sodium hydroxide, the initial pH was adjusted from 2 to 10. Then, 15 mL of adjusted solution and 30 mg of each prepared sample were added in 30-mL Erlenmeyer flask and agitated for 24 h. The solution pH was defined as pH_{pzc} when the initial pH and the equilibrium pH showed equal values.

3 Results and discussion

3.1 Potential adsorption sites for As(V) according to solution pH

The anion adsorption capacity of activated carbon is generally affected by solution pH [22]. Therefore, we assessed the potential adsorption sites for As(V) in all pH ranges using adsorption experiment data. The results of adsorption capacity at pH 2–12 are shown in Fig. 1. All samples showed the highest adsorption capacity around pH 7. We listed the highest Q_e value of each sample among the various equilibrium pH conditions in Table 2. However, the adsorption tendency in the acidic and the basic pH range was different between the CVD-treated and not-treated samples. Generally, the anion adsorption capacity in the acidic pH conditions relies on the number of basic functional groups. As examples of the basic functional groups, Ota et al. [21] reported that the π -electrons on the graphene layer can attract some protons resulting in a slight increase in adsorption site. Moreover, pyridinic nitrogen (N-6), pyrrolic nitrogen (N-5), and amine groups could become positively charged adsorption sites below certain pH which depends on their pK_a [23, 34], while

Fig. 1 Effect of the precursors on arsenic adsorption at various equilibrium pH ranges **a** HP555 **b** CVD-treated fiber precursors **c** CVD-treated activated carbon **d** KF and KF-CVD **e** BAC and BAC-CVD **f** CGP and CGP-CVD

the quaternary nitrogen (N-Q) always exists as positively charged form. Therefore, when these sites become a positive charge at certain acidic pH ranges according to their pK_a , they can act as anion adsorption sites. For the reasons, activation of carbons showed relatively high As(V) adsorption capacity at acidic pH rather than basic pH conditions. However, the pK_a values of H_3AsO_4 are 2.19, 6.94, and 11.5. For example, the dominant species of arsenate are H_3AsO_4

and $H_2AsO_4^-$ at pH 2.19. Therefore, the main species of arsenic become neutral when the solution pH showed lower than 2. The electrostatic interaction between adsorbent and adsorbate becomes repulsive. In addition, since pH was adjusted with hydrochloric acid, competition between arsenate and chloride ions causes inhibition of arsenate adsorption. In contrast, the main species of arsenic is anion at basic pH range. However, the carbon surface

charges negatively when the solution's basicity is greater than each sample pH_{pzc} . These strong basic conditions are not electrostatically appropriate for anion adsorption. Furthermore, excessive hydroxide ions also act as strong competitive ions in the basic region. To sum up, the anion adsorption is not favorable in the basic pH range.

In the case of the HP555, which is one of the strong base anion exchange resin, it has quaternary amine as functional groups [35]. From the Boehm titration results, which are shown in Table 3, the amount of basic functional groups was 0.02 mmol/g. As described in Fig. 1a, arsenate adsorption capacity of HP555 was gradually increased at pH 3–7. Adsorption capacity showed a peak at pH 7 and slowly decreased in basic pH range. Quaternary amine, the effective site of HP555, is always positively charged regardless of solution pH. Thus, N-Q is electrostatically favorable for anion adsorption, unlike N-5 and N-6 at the basic pH range. Adsorption capacity under basic pH conditions is attributed to quaternary nitrogen because it is difficult to bring protons from the solution, and excessive hydroxide ions are present in the solution. For these reasons, the adsorption under the basic pH conditions was determined as a characteristic of the N-Q rich samples.

In summary, the number of basic functional groups and increase in the content of quaternary nitrogen is important for anion adsorption in a wide pH range. However, at pH 7, some basic functional groups would not work as adsorption sites such as N-5 and N-6 (pK_a 5–6) because of their pK_a [23, 34]. For the reason, the specific surface area is also important because the carbon surface area represents the strength of the π -electrons on the graphene layer.

3.1.1 Determination of quaternary nitrogen (N-Q) content by Boehm titration

Among the potential adsorption sites for As(V) anion, N-Q showed a great effect on the adsorption capacity

in all pH ranges. Therefore, the precise measurement of N-Q content was required to determine the best adsorbent for the As(V) adsorption. Measurement of XPS is conventional way to evaluate N-Q content of the sample surface. In this study, we used Boehm titration additionally. Boehm titration is using different acidity of adsorbent and adsorbate for calculating functional groups on the surface [36]. The difference in the concentration of NaHCO_3 ($\text{pK}_a = 6.37$) before and after the reaction indicates the number of carboxy groups ($\text{pK}_a = 3\text{--}6$); the number of carboxy and lactone groups ($\text{pK}_a = 7\text{--}9$) can be calculated from concentration difference of Na_2CO_3 ($\text{pK}_a = 10.25$). Likewise, the number of carboxy, lactone, and phenol groups ($\text{pK}_a = 8\text{--}11$) can be calculated as total acidic functional groups from NaOH concentration difference ($\text{pK}_a = 15.74$). However, previous study reported that the oxygen-containing acidic functional groups were decomposed by heat treatment, and the number of carboxy groups reached zero [37]. Moreover, the temperature at which decomposition started was also reported at 100–700 °C [38]. We conducted steam activation and tCVD at 800 °C, and heat treatment was performed at 950 °C. Most of the acidic functional groups would be decomposed during CVD treatment in this study. Furthermore, HP555 showed a higher amount of carboxy groups than that of all AC samples, as shown in Table 3. To sum up, the carboxy groups reacted as the strongest adsorption sites and are adsorbing even weak anions. Hence, the carboxy groups of the CVD-treated samples could be corresponding to quaternary nitrogen. Furthermore, Boehm titration was conducted in aqueous solution. Thus, the number of N-Q (apparently as carboxy groups) can be determined as actual anion adsorption sites under the same conditions as the As(V) adsorption experiment. For these reasons, we determined the N-Q which behaved as actual adsorption sites in the aqueous conditions using the Boehm titration.

Table 3 Result of the Boehm titration and pH_{pzc} value

Sample name	Total acidic functional groups (mmol/g)	Carboxy or N-Q* (mmol/g)	Lactone (mmol/g)	Phenol (mmol/g)	Total basic functional groups (mmol/g)	pH_{pzc}
PhR-CVD	1.42	0.200	0.050	1.17	0.338	8.5
Pyromex-CVD	1.68	0.133	0.042	1.51	0.875	9.0
KF	2.00	0.094	0.019	1.92	0.360	5.6
KF-CVD	1.38	0.283	0.050	1.05	1.310	9.1
BAC	1.48	0.000	0.333	1.15	0.375	8.2
BAC-CVD	2.27	0.019	0.065	2.08	0.775	9.8
CGP	3.28	0.383	0.433	2.47	− 0.100	3.1
CGP-CVD	2.64	0.263	0.025	2.35	0.237	9.5
HP555	2.45	2.000	0.196	0.25	0.017	–

*Carboxy groups represent N-Q only in case of CVD-treated samples

3.2 Surface properties of the prepared samples

3.2.1 Pore structure

Activation process was not conducted on phenol resin (PhR) and PAN-based carbon fiber (Pyromex), so extremely low specific surface area was observed as 2 and 5 m²/g, respectively. In our previous study [22], the untreated PhR showed no adsorption capacity even at pH 7, which was the best pH condition for As(V) adsorption. Therefore, we compared only CVD-treated samples in case of fabric precursors. On the other hand, activated carbon materials showed at least 1340 m²/g of S_{BET} and noticeable adsorption capacity at pH 7, so we compared raw material and CVD-treated samples in case of activated carbon precursors. Obtained N₂ adsorption/desorption isotherms are listed in Fig. 2. We also showed BJH desorption pore distribution curves of all samples in Fig. 3 and listed the calculated surface property parameters in Table 4. After the CVD treatment, changes in the specific surface area was dependent on the starting carbon materials. CGP-CVD showed the decreased S_{BET} after the CVD treatment, but the Q_e/S_{BET} value of CGP-CVD was the highest among the CVD-treated samples. Furthermore, all CVD-treated samples depicted increased Q_e/S_{BET} value, and prepared samples from fiber form precursors also exhibited higher Q_e/S_{BET} value than that of activated carbon raw materials. In conclusion, CVD treatment would enhance the As(V) adsorption capacity due to the introduction of nitrogen and reduction of oxygen of the sample surface.

3.2.2 Elemental composition

The manufacturer describes phenol resin (PhR) as a novoloid fiber, and its carbon, hydrogen, and oxygen content are 76, 6, and 18 wt%, respectively. Because the phenol resin had a nearly zero in nitrogen content in the structure, we employed nitrogen-rich polyacrylonitrile (PAN)-based carbon fibers (Pyromex) to investigate the effect of the nitrogen content of the fiber formed from starting carbon material. Pyromex is a carbon fiber made from white polyacrylonitrile fiber and heat treatment [39]. The nitrogen content of Pyromex was 20 wt% from our elemental analysis data.

The elemental composition of the prepared samples is exhibited in Table 5. We assumed that the prepared samples consist of carbon, hydrogen, nitrogen, oxygen, and inorganic substance. Therefore, we calculated the oxygen content from the balance. After the CVD treatment, the nitrogen content increased, and the oxygen and ash content decreased. Therefore, the increased nitrogen functional group and decreased acidic functional group due to the CVD would enhance the As(V) adsorption capacity.

Fig. 2 N₂ adsorption/desorption isotherm of prepared samples

3.2.3 Content of each nitrogen species and surface functional group

To investigate the effect of surface nitrogen species according to the solution pH, the content of each nitrogen species was quantified using XPS. The XPS spectra results (N1s) of the prepared samples are given in Fig. 4. Using the nitrogen content determined by elemental analysis, the amount of each nitrogen species was quantified and enumerated in Table 6. The number of functional groups that were determined by Boehm titration is listed in Table 3. By comparing the two results, the CVD-treated sample, which

Fig. 3 BJH desorption pore distribution curves of prepared samples

Table 4 Porous structural parameters of the prepared samples

Sample name	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D_{avg} (nm)	Q_e/S_{BET} (10^{-5} mmol/ m^2)
PhR-CVD	1300	0.547	0.540	0.008	1.69	8.23
Pyromex-CVD	1390	0.835	0.702	0.133	2.40	7.19
KF	1530	0.688	0.664	0.024	1.80	3.14
KF-CVD	1660	0.799	0.771	0.028	1.93	10.4
BAC	1340	0.612	0.572	0.040	1.83	6.42
BAC-CVD	1150	0.534	0.506	0.028	1.85	9.22
CGP	1610	1.27	0.478	0.796	3.17	2.30
CGP-CVD	883	0.563	0.320	0.243	2.55	13.4

had a larger amount of acidic carboxy groups determined by Boehm titration, showed the high N-Q content measured by XPS. However, non-treated activated carbons (KF, BAC, and CGP) would contain actual carboxy acidic groups on their surface because heat treatment (9.5HT30) was not treated on their surface. CGP did not show N-Q on their surface from the XPS data, but it showed the highest number of carboxy functional groups among all prepared activated carbon samples. Thus, only the CVD-treated samples could use the number of carboxy groups as N-Q content.

All pH_{pzc} data were listed in Table 3. CGP showed the lowest pH_{pzc} value and the negative value of basic functional groups. We assumed that the acid processes caused this negative value during their manufacturing process of CGP. On the other hand, all CVD-treated samples showed higher pH_{pzc} than 8.5. These pH_{pzc} values of the CVD-treated samples were also higher than that of raw activated carbon samples (KF, BAC, and CGP). Therefore, As(V) adsorption capacity of all CVD-treated samples was enhanced in a broader pH range than non-treated samples.

3.3 Effect of the precursor type

3.3.1 Fabric precursors

Adsorption capacity at pH 2–12 is illustrated in Fig. 1b. At pH which was below pH_{pzc} of all prepared samples, the surface of the activated carbon was positively charged due to the proton attraction of the π -electrons. Arsenic adsorption was electrostatically favorable at this pH conditions. Whereas the HP555 showed gradual increase in adsorption capacity at acidic pH, and all CVD-treated samples showed drastic increase at pH 3. This seems to be one of the results of the heat treatment. Oxygen-containing acidic functional groups are known as electron-withdrawing groups, and they diminish the π -electrons on the graphene layer. Decomposition of these acidic functional groups by annealing would enhance the π -electrons. All samples showed the highest adsorption capacity at neutral pH and decreased when the basicity

Table 5 Elemental composition of the prepared samples

Sample name	C (wt%)	H (wt%)	N (wt%)	Ash content (wt%)	O* (wt%)
PhR-CVD	89	0.51	0.52	0.42	10
Pyromex-CVD	88	0.44	1.4	0.53	9.6
KF	89	0.55	1.7	1.4	7.4
KF-CVD	90	0.23	1.9	0.33	7.1
BAC	95	0.50	0.09	0	4.2
BAC-CVD	96	0.36	0.93	0	2.3
CGP	77	2.0	0.29	4.0	17
CGP-CVD	93	0.40	2.0	1.1	3.8

*Calculated by balance

of the solution became stronger. From this tendency between pH and adsorption capacity, electrostatic characteristics of arsenate and competitive ions showed a great effect on the adsorption.

KF-CVD showed the highest adsorption capacity at any pH range. Specific surface area and nitrogen content were also higher than those of PhR-CVD and Pyromex-CVD. KF had specific surface area of 1530 m²/g, whereas PhR and Pyromex indicated S_{BET} of 2 and 5 m²/g, respectively. This porous structure of KF would enhance the contact area between aniline gas and surface. In the case of Pyromex-CVD, a decrease in nitrogen content was the greatest compared to the nitrogen content of 20% for Pyromex. The yield was also lowest (12.1%), indicating that Pyromex showed a large amount of decomposition occurred during the heat treatment. To sum up, Pyromex was not suitable as a precursor for CVD, and the newly formed nitrogen-rich surface was also expected to be peeled easily during the steam activation due to the delicate surface of Pyromex. The lowest value of the adsorption amount per specific surface area supports this idea. The yield of PhR-CVD was 40%; therefore, phenol resin showed greater rigidity against steam activation than Pyromex. On the other hand, the specific surface area was 1300 m²/g, and it was the lowest value among the KF-CVD, Pyromex-CVD, and PhR-CVD. The lowest total basic functional groups among these three samples would affect the Q_e/S_{BET} value. Low nitrogen content of the precursor would cause this result.

To summarize these three sample data, the activated carbon fibers were the best precursor because of the high specific surface area and nitrogen content after the CVD treatment. Owing to the high specific surface area, an increase in contact area between the aniline gas and the carbon structure which has rigid surface against annealing would play an important role in the CVD procedure.

Fig. 4 The nitrogen characterization (N_{1s}) of the prepared samples by XPS analysis (*KF data were referred to our previous study [26])

3.3.2 Activated carbon precursors

Surface properties of activation carbon affect the adsorption capacity. Accordingly, we added BAC, BAC-CVD, CGP, CGP-CVD data to compare the influence between surface characteristics and arsenic adsorption capacity. We illustrated adsorption capacity at pH 2–12 in Fig. 1c–f. All CVD-treated samples showed enhanced As(V) adsorption capacity at basic pH conditions. From Fig. 1a, N-Q rich HP555 shows high adsorption capacity at basic pH

Table 6 Nitrogen configuration of the prepared samples by XPS N1s peak area

Sample name	XPS peak area (N1s)				Elemental analysis Nitrogen* (wt%)	Nitrogen configuration			
	N-6 (%)	N-5 (%)	N-Q (%)	N-X (%)		N-6 (wt%)	N-5 (wt%)	N-Q (wt%)	N-X (wt%)
PhR-CVD	23	6.9	55	16	0.52	0.12	0.04	0.28	0.08
Pyromex-CVD	22	20	37	20	1.4	0.30	0.27	0.50	0.28
KF	31	46	22	0	1.7	0.53	0.79	0.38	0.00
KF-CVD	28	5.6	51	16	1.9	0.52	0.11	0.96	0.30
BAC	20	59	18	3.4	0.09	0.02	0.06	0.02	0.00
BAC-CVD	31	38	18	13	0.93	0.28	0.34	0.16	0.12
CGP	28	57	0	15	0.29	0.09	0.17	0.00	0.04
CGP-CVD	28	24	45	2.7	2.0	0.57	0.48	0.90	0.05

*Bulk nitrogen content indicated at Table 5

solutions because HP555 has quaternary amine (N-Q) function as effective sites for anion adsorption. Likewise, CVD treatment could enhance the N-Q content on the carbon surface. We discussed the difference in surface characteristics between raw materials and CVD-treated sample.

Figure 1d depicted KF and KF-CVD adsorption capacity. The pH_{pzc} value of KF was 5.6. Thus, adsorption was electrostatically unfavorable at pH 7. This parameter indicated why KF showed the maximum arsenate adsorption at pH 3 rather than 7. KF has N-Q in their surface as indicated at XPS data (Table 6) and the low concentration of competitive anion such as hydroxide would enhance arsenate adsorption at pH 7. Carboxy groups could not represent N-Q in case of the KF because heat treatment was not conducted. After the CVD treatment, the oxygen content decreased, and this result depicted oxygen-containing electron-withdrawing groups was decomposed by thermal treatment [37]. As a result, the pH_{pzc} of KF-CVD was increased to 9.1. Not only the pH condition, which was lower than pH_{pzc} , but also arsenate capacity was shown in the basic pH range, which was larger than pH_{pzc} . From the number of the carboxy groups, KF-CVD indicated the highest N-Q content among all CVD-treated samples. This newly formed quaternary nitrogen would enhance the adsorption capacity regardless of pH.

BAC showed the lowest nitrogen content among the activated carbon precursors. On the other hand, pH_{pzc} of BAC was 8.2, which was higher than pH 7. In Fig. 1e, adsorption capacities were increased steeply at pH 3. At pH 5–6, the adsorption capacity was not increased. Similar to other samples, the Q_e showed the maximum value at pH 7. From the XPS measurements (Table 6), BAC showed low N-5 and N-6 content because of the 0.1 wt% of nitrogen content. These sites accommodate the protons and become adsorption sites for anions. Accordingly, adsorption capacity at pH 5–6 was affected by these low N-5 and N-6 sites. In contrast, KF showed high N-5, and N-6 value than BAC, and the electrostatic condition of the surface

was not appropriate for anion adsorption. Therefore, KF would show low adsorption capacity at pH 5–6. Nevertheless, BAC-CVD showed 0.34 wt% of N-5 and 0.28 wt% of N-6. Since the number of carboxy groups showed the lowest value among all CVD-treated samples, the quaternization of the nitrogen would not be conducted properly. In Fig. 1e, we showed that increased N-5 and N-6 content enhanced adsorption capacity at pH 5–6. At pH 7, the adsorption capacity of BAC-CVD and BAC showed a little difference because the specific surface area was decreased to 15%, and the smallest N-Q content among all CVD-treated samples after the CVD process. At the basic pH range, the amount of arsenate adsorption increased after the CVD treatment. This is because the pH_{pzc} of BAC-CVD was 9.8, and adsorption was electrostatically favorable at the broad pH range of 2.0–9.8.

In the case of the CGP and CGP-CVD, the nitrogen content of the CGP-CVD showed the highest, but the specific surface area was decreased to 44%. Because the pH_{pzc} was 3.1, the adsorption would be electrostatically favorable at the pH is below 3.1. In this pH condition, the main species of arsenate become neutral form (H_3AsO_4); therefore, the adsorption capacity showed nearly zero at acidic pH conditions (Fig. 1f). Through the CVD treatment, oxygen-containing functional groups were decomposed, and content of the N-5 and N-6 also increased. Following these results, pH_{pzc} was also increased to 9.5, so adsorption capacity was increased in the acidic solution. At the basic pH range, which is higher than 9.5, increased N-Q value showed enhanced adsorption capacity of CGP-CVD. From the increase in the nitrogen content and decreased specific surface area between CGP and CGP-CVD, the newly formed structure would have rigidity against steam activation. From the surface properties shown in Table 4, the mesoporosity of the activated carbon would affect the tCVD efficiency. We assumed that the wide diameter of the mesopores introduced more nitrogen during the tCVD process rather than microporous carbon material.

Furthermore, this newly formed surface was hard to be activated; the specific surface area of the samples made from mesoporous precursors would be hard to broaden. The difference in the specific surface area before and after CVD treatment of KF and CGP supported this idea. From the different point of view, the mesoporous CGP showed the greatest Q_e/S_{BET} value after the CVD process because of the highest introduced nitrogen content by tCVD due to their mesoporous surface. However, the surface structure induced by the tCVD process was hard to be activated, and the decreased S_{BET} caused lower Q_e than that of the KF-CVD derived from microporous KF. In the case of BAC, it was also microporous material, but the specific surface area decreased after the CVD treatment. Figure 5 shows the steam activated samples at 800 °C and varied the introduced distilled water. After the 8ST30 treatment, KF-8ST30 showed 22% enhanced S_{BET} than that of KF, but BAC-8ST30 showed 14% enhancement from S_{BET} of BAC. Furthermore, KF-8ST50 showed 32% enhanced S_{BET} than that of KF. However, BAC-8ST50 showed only 24% enhanced S_{BET} from BAC. These results indicated that BAC had greater hardness against steam activation than KF. In case of the BAC-CVD, both newly formed surface structure which was formed by tCVD and carbon surface of the original BAC was hard to be activated. Therefore, the S_{BET} was decreased while the BAC had a microporous surface. For these reasons, activated carbon fiber was the most proper carbon material for CVD using aniline to enhance As(V) adsorption capacity.

3.4 Adsorption isotherm

We showed the Langmuir adsorption isotherm of CVD-treated samples in Fig. 6 and calculated parameters are

Fig. 5 Effect of steam activation at 800 °C on the KF and BAC (0 mL data showed S_{BET} of raw material)

Fig. 6 Langmuir adsorption isotherm of arsenic adsorption for prepared samples

listed in Table 7. Since the pH which showed the maximum adsorption capacity was narrow, we decided the equilibrium pH condition as a pH 6.6–7.0. In this range, the most of CVD-treated samples showed stable adsorption capacity. From Table 7, coefficient of determination pointed out that the Langmuir isotherm was the best match with all samples. Therefore, this result suggests that the arsenic adsorption could take place on a monolayer. In conclusion, this result supports the idea that the arsenate adsorption took place on the N-Q site, protonated π -electrons on the graphene layer, and protonated basic functional groups containing oxygen and nitrogen of the samples.

4 Conclusion

Through the current study, we showed that cellulose-based activated carbon fiber, which had a microporous surface, was the most suitable for CVD treatment as the arsenic adsorption adsorbent. Nitrogen content of the fiber-form precursors affected the basic functional groups of CVD-treated samples, so the CVD-treated samples, which were made from low nitrogen-containing precursors, showed low arsenic adsorption capacity at the acidic pH condition. Besides, if the structure after the heat treatment was easy to be destroyed by the activation process, the surface generated after the tCVD process would be lost during the activation process. As same to the data of CGP-CVD, nitrogen, which was introduced by the tCVD process, would play an essential role in the arsenic adsorption mechanism at the entire pH range. Thus, the precursor should have rigid surface against heat treatment for effective CVD treatment. In the case of the CGP, the nitrogen content increased by 1.7 wt%. Thanks to its mesoporous surface, the increase was the highest among all precursors. Still, the specific surface area of the CGP-CVD was reduced drastically because the newly formed structure

Table 7 Calculated Langmuir and Freundlich isotherm parameters of CVD-treated samples for arsenate adsorption

Sample name	Langmuir isotherm			Freundlich isotherm		
	X_m (mmol/g)	K_L (L/mmol)	R^2	K_f [(mmol/g)/(L/mmol) ^{1/n}]	1/n	R^2
PhR-CVD	0.104	31.6	0.998	0.126	0.291	0.872
Pyromex-CVD	0.060	12.2	0.956	0.056	0.224	0.889
KF-CVD	0.120	13.2	0.983	0.113	0.244	0.979
BAC-CVD	0.093	7.65	0.969	0.085	0.306	0.939
CGP-CVD	0.091	5.52	0.953	0.094	0.470	0.815

had resistant to the water activation. This rigid surface led to a decrease in basic functional groups, resulting in low adsorption capacity at acidic pH conditions. In contrast, the microporous KF showed the lowest increase in nitrogen after CVD, but the specific surface area increased compared to the other activated carbons. Furthermore, KF-CVD showed the highest N-Q value among all CVD-treated samples. As a result, the adsorption amount at the entire pH conditions increased; KF was the best precursor for the CVD process to prepare arsenic adsorbent.

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Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

Data and code availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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