

Adsorption of nitrate onto nitrogen-doped activated carbon fibers prepared by chemical vapor deposition

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Abstract—Nitrogen-doped activated carbon fibers (ACFs) were prepared by chemical vapor deposition using melamine powder and acetonitrile for introducing quaternary nitrogen on the commercial ACFs, subsequently heated at 950 °C and activated by steam. Adsorption experiments of nitrate in aqueous solution were also conducted to evaluate adsorption capacity of the prepared ACFs using ion chromatography. The amount of introduced nitrogen content and nitrogen species on activated carbon fibers was examined by CHN elemental analyzer and X-ray photoelectron spectroscopy, respectively. As a result, adsorption capacity of quaternary nitrogen-doped ACF (ST-ML-AN-ST) was 0.75 mmol/g, indicating ca. two-times higher than that of untreated ACF (0.38 mmol/g). According to the adsorption data, the Langmuir isotherm model was the best fit. The prepared samples were also regenerated using hydrochloric acid. After regeneration, the adsorption capacity of the nitrogen-doped ACF (ST-ML-AN-ST) showed ca. 80% on average, implying that a portion of nitrates was adsorbed on the prepared ACFs irreversibly.

Keywords: Nitrate, Quaternary Nitrogen (N-Q), Adsorption, Activated Carbon Fibers, Chemical Vapor Deposition

INTRODUCTION

Excessive nitrate released from industrial, agricultural and livestock wastewater has polluted various water sources, and may cause environmental problems including eutrophication [1]. In addition to these environmental risks, nitrate is reduced into nitrite in the digestive system and causes risks to human health. Nitrite reacts with hemoglobin and forms methemoglobin, which has no oxygen binding ability. For this reason, it mainly causes infant methemoglobinemia. Not only methemoglobinemia, but also symptoms such as headache, fatigue, dizziness, syncope, and seizures are also reported [2]. In addition, nitrites produce N-nitrosamines, which are a precursor of carcinogens [3]. Therefore, WHO has set the nitrate standard of drinking water to be 50 mg-NO₃/L or less [4].

As a method of removing nitrate from water sources, electrodiagnosis [5], reverse osmosis [6], biological denitrification [7,8], and adsorption [9-11] using activated carbon and ion exchange resin could be available. Among these, adsorption is simple and can be conducted at low cost [12]. The activated carbon is widely used for the adsorption of organic substances due to its porous structure and large specific surface area, but the surface of the activated carbon is hydrophobic, so it is not suitable for removing ionic substances such as nitrate and phosphate ions [13].

Recent studies have reported that the increase in the content of quaternary nitrogen on the activated carbon surface enhances the adsorption capacity of nitrate ions [9,11]. Since the quaternary nitro-

gen introduced on the surface of the activated carbon fiber (ACF) acts as positively charged adsorption sites on the carbon, it is advantageous for adsorption of nitrate. To introduce the quaternary nitrogen on the activated carbon surface, Ghadiri et al. [9] conducted surface modification with epichlorohydrin and triethylamine, and Goto et al. [11] also performed methylation of surface nitrogen with methyl iodide. It has been reported that the quaternization of nitrogen progresses by thermal decomposition of nitrogen-containing carbon fiber at a temperature of 500 °C or more [14]. Accordingly, it is expected that the quaternary nitrogen also increases as the nitrogen content on the surface of activated carbon increases.

In this study, we introduced nitrogen on the surface of commercial ACFs by chemical vapor deposition (CVD) and quaternization of introduced nitrogen by heating at 950 °C to enhance the nitrate adsorption capacity. Since activated carbon has large specific surface area, the CVD process could be effective. Acetonitrile [15] and melamine, which contain unsaturated carbon in their structure and high nitrogen content (34 wt% and 66 wt%, respectively) were used for CVD process. In addition, the specific surface area, elemental analysis, nitrogen configuration, Boehm titration and the pH of the point of zero charge (pH_{pzc}) of the prepared samples were determined, and the relationship of these parameters and nitrate adsorption capacity was evaluated.

MATERIALS AND METHODS

1. Reagents

All the reagents except melamine powder used in this study were analytical grade and used without purification. Purity of the melamine was 98.0% in minimum and used without further purification.

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Commercial activated carbon fiber KF1500LDA (KF) was purchased from Toyobo Co. Ltd., Japan. The manufacturer describes the KF as a carbonated fiber produced from cellulosic fibers that has a micro-porous structure. KF was dried at 110 °C for 30 minutes before treatment.

2. Adsorbent Preparation

Heat treatment and steam activation were conducted as pre-treatment and post-treatment, respectively. In a tubular reactor, samples were heated at 950 °C for 30 minutes under a helium flow. We used quartz pipe as a reactor, 28 mm o.d.×24 mm i.d.×0.60 m length in size. Subsequently, 50 mL of distilled water was introduced for 100 minutes at 800 °C. Conditions of heat treatment and steam activation were determined by our previous study [16]. The samples conducted in these processes were named as ST.

Chemical vapor deposition (CVD) was performed using melamine and acetonitrile. Chemical vapor deposition using melamine was conducted in an electric furnace. Two grams of melamine powder were added in a crucible and put 0.5 g ACFs on the melamine powder. The crucible was covered with a lid and heated at 400 °C for four hours under a self-generated atmosphere to vaporize the melamine powder. Chemical vapor deposition using acetonitrile was conducted in a tubular reactor. Two grams in maximum of the samples were inserted in the quartz pipe and heated at 800 °C. Then, 40 mL of acetonitrile was introduced for three hours under a helium flow. The CVD-treated samples using melamine and acetonitrile were referred to as ML and AN, respectively.

Through this process, ST, ST-AN-ST, ST-ML-ST and ST-AN-ML-ST were prepared. All prepared samples were washed with hot distilled water and dried at 110 °C overnight. Finally, the samples were cut into 0.5 cm×0.5 cm for homogenization.

3. Adsorption Studies

Adsorption experiments for nitrate were performed using NaNO₃ aqueous solution. The initial concentration of nitrate was varied from 0.323 to 6.45 mmol/L. In a 30 mL Erlenmeyer flask, 30 mg of prepared samples and 15 mL nitrate solution were added and equilibrium solution pH (pH_e) was adjusted to 3 using hydrochloric acid. The pH_e condition was determined by our previous study [16], which indicated that pH_e 3 was optimal for nitrate adsorption. The solution pH was measured with pH meter (D-51, Horiba). The mixture was agitated at 100 rpm and 25 °C for 24 hours. Nitrate concentration was determined by ion chromatograph (ICS-1100, Nippon Dionex KK), and adsorption amount at the equilibrium state was calculated by the following equation:

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

where C₀ and C_e represent the initial nitrate and the equilibrium nitrate concentrations (mmol/L), respectively; v represents solution volume (mL) and w indicates weight of adsorbent (mg). Adsorption isotherm studies were also performed. Langmuir and Freundlich isotherm models were applied to evaluate parameters of each isotherm.

4. Adsorbent Properties

Elemental composition was determined by CHN elemental analyzer (PE2400II, Perkin Elmer). We assumed that the ACFs were composed of carbon, hydrogen, nitrogen, and oxygen; therefore, oxy-

gen content of the ACFs was calculated by balance. Nitrogen species on the prepared samples were characterized by X-ray photoelectron spectroscopy (Model-1800, ULVAC-PHI). Introduced nitrogen was assumed to be pyridinic nitrogen (N-6), pyrrolic nitrogen (N-5), quaternary nitrogen (N-Q) and pyridine-N-oxide (N-X), which were reported by Pels et al. [14].

Boehm titration method was used to determine the amount of surface acidic and basic functional groups [17]. Solutions of 0.1 mol/L NaOH and 0.1 mol/L HCl were prepared, and 25 mL of each solution and 50 mL of each sample were added in a 100 mL Erlenmeyer flask. The flasks were agitated for four days at room temperature. Then, 5 mL of each solution was titrated with 0.05 mL HCl. In case of the 0.1 mol/L NaOH, 10 mL of 0.1 mol/L NaOH was additionally added to perform back titration. We assumed that NaOH and HCl were neutralized by acidic and basic functional groups, respectively.

The pH_{pzc} of the prepared samples was evaluated by the following procedure. The initial pH of distilled water was adjusted from 1 to 11 using hydrochloric acid and sodium hydroxide. Then, 15 mL of each solution and 30 mg of each prepared sample were added in 30 mL Erlenmeyer flask and agitated for 24 hours. The solution pH was defined as pH_{pzc} when the initial pH and the equilibrium pH showed equal values [18].

Textural properties of the prepared nitrogen-doped ACFs were evaluated by BET method. Prepared samples were dried at 110 °C overnight and outgassed at 300 °C for an hour. BET measurement was conducted using nitrogen gas adsorption and desorption isotherms at -196 °C (BELSORP-mini II, MicrotracBEL). The specific surface area (S_{BET}) and average pore size (D_{ave}) of the samples were calculated by BET method. The total pore volume (V_{total}) was calculated from the maximum nitrogen adsorption capacity at a relative pressure of 0.99. The micropore volume (V_{micro}) was calculated by SPE method using α_s plots. The mesopore volume V_{meso} (cm³/g) was calculated by difference between V_{total} and V_{micro} [19].

RESULTS AND DISCUSSION

1. Adsorption Isotherms

In this study, Langmuir and Freundlich isotherm models were applied to fit the nitrate adsorption data on the prepared ACFs. Langmuir isotherm model is represented as the following equation:

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

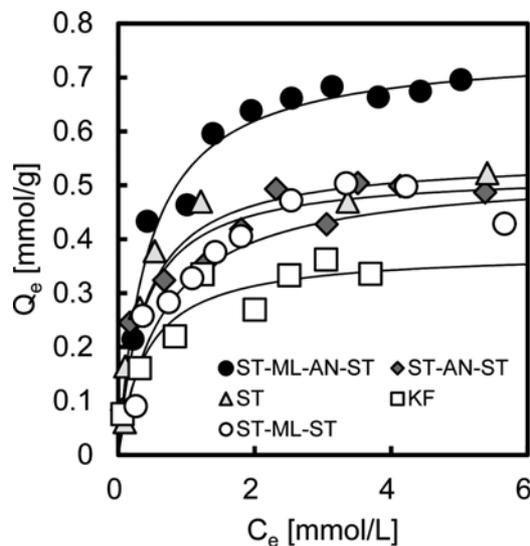
where C_e refers to the nitrate concentration (mmol/L) at equilibrium, K_L represents the Langmuir isotherm constant related to the adsorption energy, Q_e and Q_m are the adsorption capacity at the equilibrium and maximum adsorption capacity, respectively [20]. When the prepared ACFs well fitted the Langmuir isotherm model, the adsorption efficiency at certain initial concentrations could be evaluated by dimensionless separation factor R_L. Separation factor R_L is expressed as the following equation:

$$R_L = \frac{1}{1 + K_L C_0}, \quad (3)$$

where K_L is the Langmuir isotherm constant, and C₀ is the initial

Table 1. Langmuir and Freundlich parameters for adsorption of nitrate on the ACFs

Sample name	Langmuir isotherm				Freundlich isotherm		
	X_m [mmol/g]	K_L [L/mmol]	R_L	R^2	K_f [(mmol/g)(L/mmol) ^{1/n}]	1/n	R^2
KF	0.38	2.45	0.086-0.66	0.971	0.23	0.37	0.941
ST	0.55	2.62	0.056-0.64	0.990	0.34	0.42	0.736
ST-ML-ST	0.52	1.73	0.081-0.57	0.956	0.59	0.54	0.801
ST-AN-ST	0.52	2.82	0.053-0.62	0.988	0.33	0.37	0.892
ST-ML-AN-ST	0.75	2.30	0.064-0.40	0.996	0.46	0.32	0.848

**Fig. 1. Adsorption isotherm of nitrate ion for prepared activated carbon fibers (ACFs). Solid lines; Langmuir isotherm fitting.**

nitrate concentration of solution. The adsorption is irreversible when $R_L=0$, favorable when $0 < R_L < 1$, and linear when $R_L=1$, unfavorable when $R_L > 1$ [20].

Freundlich isotherm model can be represented as the following equation:

$$Q_e = K_f C_e^{1/n}, \quad (4)$$

where K_f and n represent the Freundlich isotherm constant. K_f is related to adsorption capacity and $1/n$ related to heterogeneity of the surface [21].

The adsorption isotherms for prepared samples are shown in Fig. 1. Table 1 shows the calculated Langmuir and Freundlich parameters. Coefficient of determination R^2 indicates that the Langmuir

Table 2. Elemental composition of the ACFs

Sample name	C [wt%]	H [wt%]	N [wt%]	O* [wt%]
KF	89	0.55	1.7	9.2
ST	93	0.39	0.91	5.8
ST-ML-ST	84	0.41	3.3	12
ST-AN-ST	90	0.19	3.6	6.6
ST-ML-AN-ST	89	0.23	4.3	7.0

*Calculated by balance

isotherm was the best match with all samples. From the X_m and R_L obtained from Langmuir isotherm model, every preparation method enhanced nitrate adsorption, and all prepared samples were appropriate for the favorable nitrate adsorption.

2. Adsorbent Properties

Elemental composition and nitrogen configuration of the prepared ACFs are shown in Tables 2 and 3, respectively. The XPS spectra are depicted in Fig. 2. In comparison with KF and ST, the content of oxygen and nitrogen decreased after steam activation. All CVD-treated samples also showed higher nitrogen content and greater adsorption capacity than those of KF and ST. Not only the nitrogen content in the pristine material, but also amount of quaternary nitrogen (N-Q) was increased.

Results of the Boehm titration and pH_{pzc} are indicated in Table 4. All prepared ACFs presented higher pH_{pzc} value than KF. When the solution pH is lower than pH_{pzc} , the surface of ACFs charged is positive. Positively charged surfaces are favorable for anion adsorption; therefore, we could assume that all treated samples would be favorable for nitrate adsorption at pH_e 3. Content of basic functional groups showed significant differences by at least 2.4-times among the prepared samples. All results indicated that steam activation enhanced the basicity of the surface. However, ST-ML-ST showed the lowest increasing rate of the surface basicity, implying

Table 3. 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%]
KF	31	46	22	0	1.7	0.53	0.79	0.38	0.00
ST	75	0	25	0	0.91	0.68	0.00	0.23	0.00
ST-ML-ST	31	32	21	16	3.6	1.11	1.15	0.77	0.57
ST-AN-ST	35	8	12	45	3.3	1.16	0.26	0.40	1.48
ST-ML-AN-ST	38	16	42	3	4.3	1.65	0.71	1.81	0.13

*Bulk nitrogen content was indicated in Table 2

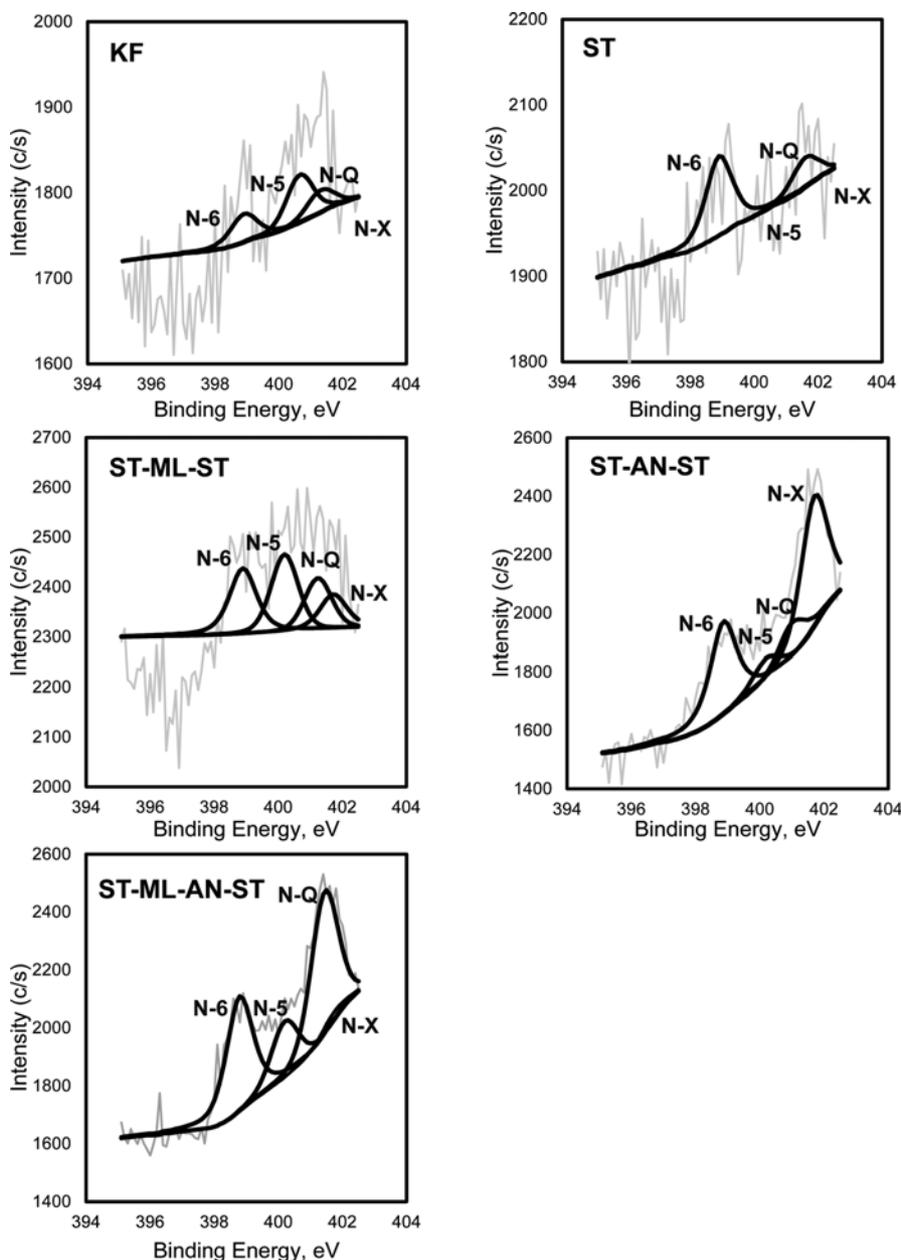


Fig. 2. The nitrogen characterization (N1s) of the prepared samples by XPS analysis (Model-1800, ULVAC-PHI).

Table 4. Comparison of the nitrate ion adsorption capacities of the various adsorbents

Sample name	Acidic functional groups [mmol/g]	Basic functional groups [mmol/g]	pH _{pzc}
KF	0.21	0.20	4.6
ST	0.21	0.63	7.5
ST-ML-ST	0.20	0.48	7.4
ST-AN-ST	0.21	0.93	7.3
ST-ML-AN-ST	0.18	1.07	7.0

melamine CVD was not conducted in inert gas; therefore, basic functional groups could be oxidized during the CVD process. Since

melamine is hard to dissolve into water or other organic solvents, it is hard to introduce nitrogen in the experimental system continuously. According to the results of XPS, ST-ML-ST indicated that melamine could indeed introduce quaternary nitrogen (N-Q) on the ACFs surface, but it might not be deposited deep inside the pore.

Porous structural parameters of activated carbons are shown in Table 5. After the acetonitrile CVD process, the porous structure could be sealed by the newly formed nitrogen-rich surface. Therefore, steam activation or other activation method as a post-treatment is required after the CVD process. In the case of ST-ML-ST, the amount of melamine introduced might be insufficient, so it had larger specific surface area than ST.

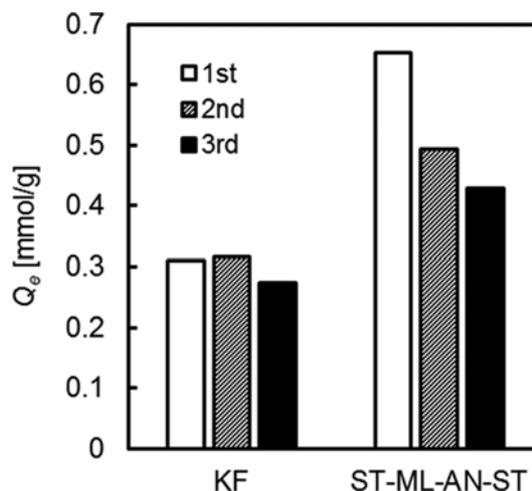
ST-ML-AN-ST showed the largest adsorption capacity in this study. Although ST-ML-AN-ST had lower specific surface area than

Table 5. Porous structural parameters of the ACFs

Sample name	S_{BET} [m ² /g]	V_{total} [cm ³ /g]	V_{micro} [cm ³ /g]	V_{meso} [cm ³ /g]	D_{ave} [nm]
KF	1540	0.688	0.664	0.024	1.79
ST	2220	1.162	1.123	0.039	2.09
ST-ML-ST	2380	1.197	1.190	0.008	2.01
ST-AN-ST	790	0.370	0.354	0.016	1.87
ST-ML-AN-ST	1180	0.568	0.544	0.024	1.93

KF and ST, quaternary nitrogen (N-Q) content and surface basic functional groups were the highest among all prepared samples. CVD-treated samples would have nitrogen-rich surface, and the introduced nitrogen species would be converted into quaternary nitrogen (N-Q) by heat treatment. In contrast, ST-ML-ST and ST-AN-ST exhibited almost the same value in adsorption capacity with KF and ST. The S_{BET} of ST was similar to that of ST-ML-ST. ST had surface basic functional groups of 0.63 mmol/g, while ST-ML-ST showed 0.48 mmol/g. Ota et al. [22] reported that π -electrons on the graphene layer can accommodate some protons resulting in a slight increase in adsorption capacity. For this reason, ST-ML-ST would show the similar adsorption capacity, whereas the quaternary nitrogen (N-Q) content was 3.3-times higher than ST. In case of ST-AN-ST, surface functional groups and quaternary nitrogen content (N-Q) were ca. 1.5- and 1.7-times higher than those of ST, respectively. However, ST-AN-ST had S_{BET} of 780 m²/g, only 36% of ST. It could be assumed that the specific surface area of nitrogen-introduced ACFs also played an important role for nitrate adsorption. Although ST-ML-AN-ST showed S_{BET} of 1,180 m²/g, the adsorption capacity of ST-ML-AN-ST was ca. 1.4-times higher than ST. Therefore, further experiments for activation methods will be required.

Comparisons of nitrate ion adsorption capacities of the various adsorbent are shown in Table 6. ST-ML-AN-ST showed greater adsorption capacity than other adsorbents except Z6-Q. Activated carbon prepared from melamine sponge and modified by methyl iodide (Z6-Q) showed higher adsorption capacity than ST-ML-AN-ST, but Z6-Q required raw material possessing high nitrogen content. In this study, the results pointed out that CVD can introduce various forms of nitrogen including N-Q on the ACFs. Therefore,

**Fig. 3. Regeneration of KF and ST-ML-AN-ST for nitrate adsorption (initial concentration: 3.23 mmol/g).**

a combination of methyl iodide modification and CVD treatment would resolve the limits of Z6-Q method and enhance the adsorption capacity because of high N-Q content.

3. Regeneration Study

As mentioned, the adsorption method is simple and can be conducted at low cost. Regeneration of adsorbent could emphasize these advantages and be simply conducted with high concentration of hydrochloric acid. Regeneration of the N-Q-rich material would proceed according to the following equation [9]:



Therefore, a regeneration study was performed by using 1 M HCl aqueous solution. The mixture of ACFs after adsorption experiment and HCl was agitated at 100 rpm, 25 °C for 24 hours. ST-ML-AN-ST was used due to the highest nitrate adsorption capacity in this study. Fig. 3 reveals the adsorption capacity of the regenerated ACFs. When KF showed 78% of the previous adsorption capacity in the third cycle, ST-ML-AN-ST showed 76% and 85% of the previous adsorption capacity after the second and third cycles, respectively. There were various adsorption sites including N-Q on the surface of the prepared ACFs. Therefore, this result implies that a portion of nitrates strongly interacted with some adsorption sites,

Table 6. Comparison of the nitrate ion adsorption capacities of the various adsorbents

Adsorbent	Adsorption capacity (from Langmuir isotherm) [mmol/g]	pH	Adsorbent dosage [g/L]	References
Activated carbon prepared from melamine sponge and modified by methyl iodide (Z6-Q)	0.81	3-4	2.0	[11]
PAN-based ACF prepared by heat treatment (PYR-8ST20-9.5HT30)	0.72	3	2.0	[16]
Biochar made from soybean (SB600)	0.44	3	1.0	[23]
Cationic polymer-modified granular activated carbon (CPMG)	0.43	6.5-6.8	2.5	[24]
Activated carbon derived from <i>Pinus canariensis</i> and post-treated by urea (PC-PU)	0.45	2	1.0	[25]
ST-ML-AN-ST	0.75	3	2.0	This study

which make irreversible adsorption.

CONCLUSIONS

Nitrogen-doped activated carbon fibers (ACFs) were prepared by chemical vapor deposition using melamine powder and acetonitrile for introducing nitrogen on the surface, subsequently heated at 950 °C and activated by steam. The conclusions can be summarized as follows.

- Langmuir isotherm models were well fitted to all the CVD-treated samples.
- CVD treatment using acetonitrile and melamine could effectively introduce quaternary nitrogen (N-Q) on the surface of ACFs.
- Steam activation after the CVD treatment enhanced adsorption capacity compared with the sample conducted only steam activation.
- CVD-treated samples could be regenerated with high concentration of hydrochloric acid.

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