



Research Article

Adsorption of nitrate from aqueous phase onto nitrogen-doped activated carbon fibers (ACFs)

Motoi Machida^{1,2}  · Pyunghwa Yoo³ · Yoshimasa Amano^{1,2}

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Abstract

Rayon-based activated carbon fiber (ACF) was modified with several methods: acetonitrile thermal chemical vapor deposition at 800 °C (8AN) to dope nitrogen element on carbon surface, heat treatment at 950 °C (9.5HT) to convert doped nitrogen species into quaternary nitrogen (N-Q) and steam activation at 800 °C (8ST) to additionally develop pore structure. The modified samples were evaluated as adsorbents for the removal of nitrate from NaNO₃ aqueous solution at equilibrium solution pH (pH_e) around 3.0. Sequential modification of ACF with 8AN, 9.5HT and 8ST achieved the greatest adsorption capacity at 0.7 mmol/g in all prepared samples. The modified adsorbent was probably included in the greatest group in nitrogen-doped carbonaceous adsorbents for nitrate removal. To inspect the high adsorption capacity, specific surface area, elemental analysis and X-ray photoelectron spectroscopy measurements were conducted comparing with the other prepared adsorbents. Based on the data analysis, some specific surface area and N-Q might play an important role in the adsorptive removal of nitrate.

Keywords Nitrate/nitrite anion adsorption · Activated carbon fiber · Nitrogen doping · Acetonitrile thermal CVD

1 Introduction

Phosphorous and nitrate/nitrite as well as ammonia have been playing a decisive role as fertilizers in increasing wheat production [1]. However, nowadays, excess fertilizing application leads to eutrophication of lakes and pond, red tide in costal sea area and nitrate contamination of groundwater that are frequently found worldwide. Once a large amount of ammonia was produced in industrial scale, it will be released into environment and easily oxidized to nitrate/nitrite resulting in environmental loading in lake, groundwater and costal sea area [2]. At first, the nitrate/nitrite problems were found in developed countries, but the contamination was also expanded to developing countries even more severely [3]. Particularly, removal of nitrate from drinking water is one of the most important technologies to be established. US-EPA

together with other organizations demonstrated that adsorptive removal is one of the most feasible treatments for the safe drinking water supply [4–6]. Sometimes, activated carbon (AC) and ion-exchanger cartridge is set at the faucet as a water-purifying device in home kitchen. AC is principally used for removal of organic pollutants, while ion exchanger is supplied for ionic contaminants like Pb(II), Cd(II) and nitrate/nitrite.

In general, carbonaceous materials have robustness against heating and acid/basic conditions, thereby carbons are expected to be easily regenerated with some treatments compared to polymer substances. In our previous study, oxidized activated carbons (ACs) and activated carbon fibers (ACFs) were successfully prepared to reduce the concentration of cationic contaminants as Pb(II), Cd(II), Ni(II) and other heavy metal ions in aqueous phase [7, 8]. However, development of carbonaceous adsorbents to

✉ Motoi Machida, machida@faculty.chiba-u.jp | ¹Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan. ²Safety and Health Organization, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan. ³Graduate School of Science and Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan.



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uptake anionic pollutants as As(III), Cr(VI), phosphate, nitrate, etc., are still a challenging study, because adsorption capacities are far below compared to ion-exchange resin [9, 10]. In our preliminary study, nitrogen doping was repeatedly carried out using various procedures to increase the adsorption capacities of anions. At first, oxidized ACs were treated with ammonia to efficiently enhance the adsorption capacity of nitrate [10]. Next melamine form was used as a starting material for carbonization and methylation of nitrogen elements using methyl iodide for pyridinic (N-6) and pyrrolic (N-5) type nitrogen to yield quaternary nitrogen (N-Q) on carbonized melamine for the nitrate removal [11]. Air-stabilized polyacrylonitrile (PAN) fiber was also supplied for the preparation of nitrate adsorbent, and 0.6 mmol/g of nitrate density could be achieved by steam activation at 800 °C and heat treatment at 950 °C in an electric furnace [12]. Recently, we have also investigated thermal chemical vapor deposition (CVD) to dope nitrogen into a rayon-based activated carbon fiber (ACF), namely KF1500, and large capacities of 0.6–0.7 mmol/g of nitrate adsorption by the carbonaceous adsorbent could be successfully attained as well [13, 14]. In the present study, some physical and chemical properties on carbon surface were examined to interpret the large adsorption capacities of nitrogen-doped ACFs.

2 Experimental

2.1 Preparation of adsorbent and adsorption experiments

Rayon (cellulose)-based activated carbon fiber KF1500LDA (hereafter denoted as KF) was purchased from Toyobo Co. Ltd., Japan. Although a part of procedures for the modification of KF had already been briefly described in the previous proceedings [13], detailed methods could be described as follows. Ca. 2 g of felt-shaped KF was placed in quartz tube of 25 ϕ inner diameter and inserted into a horizontal cylinder-shaped electric furnace. Thermal chemical vapor deposition (CVD) was made by slowly sending acetonitrile solution to 100 mL/min helium flow in the quartz tube using tube pump and heated up to 800 °C at KF sample for doping nitrogen element onto graphene sheets. KF modified with the acetonitrile CVD is referred to as KF-8AN x in which x is volume of acetonitrile sent to the KF. For example, KF-8AN20 represents that KF was treated with 20 mL acetonitrile at 800 °C. Heat treatment of KF sample was conducted at 950 °C under 100 mL/min helium flow as well. When resultant sample is denoted as KF-9.5HT30, it means KF sample has been heat-treated at 950 °C for 30 min. Likewise, steam activation was performed to develop the pore structure by

injecting pure water drop by drop into the helium flow and completely heating up to 800 °C to become super heat steam. KF-8ST30 indicates that KF has been activated by the 800 °C super heat steam generated from 30 mL pure water in total. KF was modified using some combinations of above methods; for instance, KF-8AN20-9.5HT30-8ST30 represents sequential treatments of 20 mL acetonitrile thermal CVD at 800 °C, heat treatment at 950 °C for 30 min in helium flow and finally steam activation at 800 °C injecting 30 mL water. An *n*-heptane (C7) instead of acetonitrile (AN) was also loaded onto KF by thermal CVD to compare with AN thermal CVD.

Thirty milligrams of the modified sample and 15 mL of sodium nitrate (NaNO₃) solution were mixed and agitated for at least 12 h, because 6 h was confirmed to be sufficient to achieve the equilibrium state of NO₃⁻ adsorption in our preliminary kinetic study. The initial NaNO₃ concentration was 3.23 mmol/L (200 mg-NO₃⁻/L). The equilibrium solution pH (pH_e) was adjusted to about 3 by use of 0.1 M HCl solution, because maximum adsorption amounts of nitrate could be always observed at pH_e 3, in which differences in adsorption capacities were easily distinguished among adsorbents [10–12]. The solution pH was measured with portable pH meter, HORIA model D-51. Concentration of NO₃⁻ in the equilibrium solution was determined by IC (ion chromatograph), Nippon Dionex KK, model ICS-1100. The adsorption amount on the adsorbent at equilibrium state Q_e in mmol/g was calculated with Eq. (1):

$$Q_e = (C_0 - C_e) \times \frac{V}{W}, \quad (1)$$

where C_0 and C_e are initial and equilibrium NO₃⁻ concentration in mmol/L, respectively, and v and w are 15 mL solution volume and 30 mg adsorbent weight. Bead-shaped granular activated carbon (BAC) was obtained from Kureha Co., Ltd., and used as a reference material for adsorption.

2.2 Characterization of the carbonaceous adsorbents

To inspect the relationship between adsorption amounts of nitrate and modification procedures of KF ACF, surface and bulk characterizations were carried out. Specific surface area and pore distributions were calculated from N₂ adsorption and desorption isotherms at -196 °C using BELSORP-mini II surface analyzer (MicrotracBEL Corp., Japan). The specific surface area was measured by BET theory (S_{BET}) and SPE method using α_s plots (S_{α_s}) [15]. Total pore volume (V_{total}) was determined from N₂ volume adsorbed at relative pressure (p/p_0) at 0.995. Micropore volume (V_{micro}) was estimated from the α_s plots with SPE methods, and then mesopore volume (V_{meso}) could be

obtained by just subtracting V_{micro} from V_{total} . CHN bulk elemental analysis was performed by PerkinElmer PE2400 CHN analyzer. Oxygen content was calculated by balance on the assumption that all other elements except C, H and N would be O (oxygen). X-ray photoelectron spectroscopy (XPS) analysis was conducted with XPS, PHI1800, ULVAC PHI, using Al- K_{α} line to obtain N(1s) spectra and separated them into pyridine type (N-6), pyrrole (N-5), quaternary

(N-Q) and pyridine-N-oxide (N-X) signals by post-deconvolution analysis [16].

3 Results and discussion

Figure 1 shows NO_3^- adsorption amounts in mmol/g at the equilibrium state for 10 different carbonaceous adsorbents, pristine BAC, KF and KF treated with acetonitrile, heat treatment, super heat steam and their combinations, together with their equilibrium solution pH (pH_e). The 10 samples were selected out of more than 300 KF modified samples, in which both trial-and-error experiments were included, and in our experimental system, the coefficient of variation (C_v) could be controlled to be $< 5\%$ in reproducibility for the preparation of adsorbents followed by adsorption experiments of nitrate. Table 1 displays comparison of nitrate adsorption capacities of ACs and ACFs obtained in our previous and present works with those reported by other researchers in recent years. Presently, the prepared KF ACF in this study seems to be one of the excellent adsorbents for nitrate among ACs and ACFs.

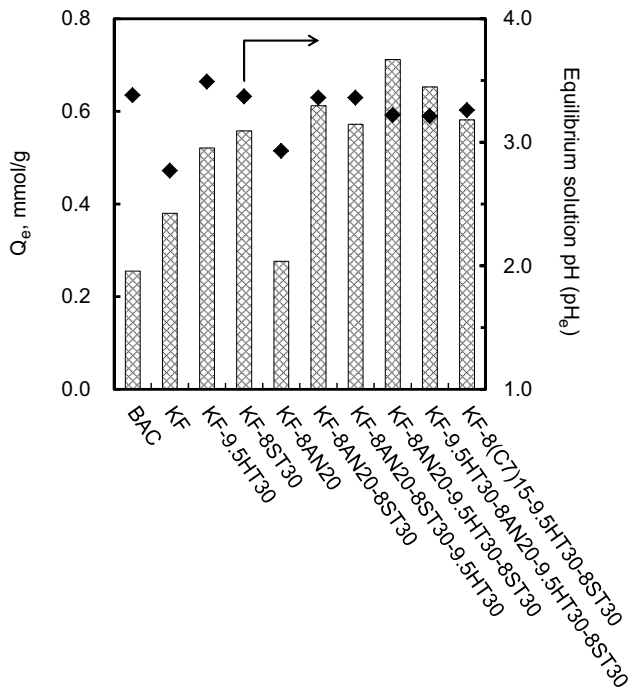


Fig. 1 Adsorption amounts of nitrate onto bead-shaped granular activated carbon (BAC) and KF1500 activated carbon fibers (ACFs) modified with thermal chemical vapor deposition (CVD) at 800 °C using 20 mL acetonitrile (8AN20), heat treatment at 950 °C for 30 min (9.5AN30), steam activation at 800 °C using 30 mL water (8ST30) and their combination such as 8AN20-9.5HT30-8ST30 together with corresponding equilibrium solution pH (pH_e). The initial nitrate concentration is 200 mg- NO_3^-/L (3.23 mmol/L). Adsorption conditions: amount of adsorbent of 30 mg and solution volume of 15 mL at r.t. at 100 rpm for 12 h or more

The results of textural and surface properties and elemental analysis of the prepared samples are summarized in Table 2. In the original KF (KF1500), although KF was mainly originated from nitrogen-free rayon (cellulose)-based ACF, a small amount of nitrogen (1.7%) could be detected. This is caused by a partly mixing nitrogen-containing flame retardant in the industrial production process of KF (KF1500). The quantitative deconvolution of XPS spectra of nitrogen doped on six selected KF series is given in Table 3 assuming that N content (%) in Table 2 would be equal to total surface nitrogen, together with the original N(1 s) XPS spectra as partly displayed in Fig. 2.

As can be clearly shown in Fig. 1, adsorption amounts of nitrate were varied from 0.25 to 0.71 mmol/g. Although the adsorption amounts are not simply proportional either to specific surface area (Table 1) or to surface nitrogen content including quaternary nitrogen (N-Q, Table 3), both specific surface area and nitrogen seem to play an

Table 1 Comparison of nitrate (NO_3^-) adsorption capacities of activated carbons (ACs)

| Sample | Adsorption capacity (mmol/g) | pH_e | References |
|--|------------------------------|---------------|-------------------------|
| Calgon F400 oxidized and outgassed at 1000 °C | 0.18 | 6 < | Our previous study [17] |
| Kureha BAC oxidized and ammonization at 950 °C | 0.54 | 3 | Our previous study [10] |
| Modified GAC | 0.35 | 7 | [18] |
| Norit GCN 1240 activated carbon | 0.24 | 4 | [19] |
| Activated carbons made from pine cones | 0.45 | 2 | [20] |
| PAN AC fiber | 0.61 | 3 | Our previous study [12] |
| Nitrogen-doped KF1500 AC fiber | 0.71 | 3 | This study |

Table 2 Properties of activated carbon (AC; BAC) and activated carbon fiber (ACF; KF series)

| Sample name | Textural and surface properties | | | | | Bulk elemental composition | | | |
|--------------------------------|--------------------------------------|------------------------------------|--|--|--------------------|----------------------------|--------------|--------------|-------------------------|
| | S_{BET} (m ² /g) | S_{α_s} (m ² /g) | Total pore volume (cm ³ /g) | Micro pore volume (cm ³ /g) | Pore diameter (nm) | Carbon (%) | Hydrogen (%) | Nitrogen (%) | Oxygen ^a (%) |
| BAC | 1360 | 1090 | 0.62 | 0.58 | 1.8 | 94.0 | 0.7 | 0.4 | 5.0 |
| KF | 1540 | 1510 | 0.69 | 0.66 | 1.8 | 88.4 | 0.6 | 1.7 | 9.3 |
| KF-9.5HT30 | 1300 | 1360 | 0.56 | 0.54 | 1.7 | 89.2 | 0.3 | 1.4 | 9.1 |
| KF-8ST30 | 1960 | 1890 | 0.94 | 0.90 | 1.9 | 93.5 | 0.3 | 1.1 | 5.1 |
| KF-8AN20 | 10 | 8 | 0.01 | 0.01 | 4.9 | 92.3 | 0.3 | 4.2 | 3.2 |
| KF-8AN20-8ST30 | 1190 | 1270 | 0.51 | 0.50 | 1.7 | 82.7 | 0.7 | 2.5 | 14.1 |
| KF-8AN20-8ST30-9.5HT30 | 1340 | 1380 | 0.59 | 0.57 | 1.8 | 88.3 | 0.7 | 2.2 | 8.8 |
| KF-8AN20-9.5HT30-8ST30 | 1560 | 1620 | 0.70 | 0.68 | 1.8 | 85.5 | 0.5 | 2.2 | 11.9 |
| KF-9.5HT30-8AN20-9.5HT30-8ST30 | 1730 | 1790 | 0.77 | 0.74 | 1.8 | 84.0 | 0.8 | 1.8 | 13.4 |
| KF-8(C7)15-9.5HT30-8ST30 | 1340 | 1400 | 0.59 | 0.56 | 1.8 | 92.7 | 0.3 | 0.8 | 6.2 |

^aCalculated by difference

Table 3 Deconvolution of nitrogen species of ACFs (KF series)

| Sample name | N-6 (%) | N-5 (%) | N-Q (%) | N-X (%) |
|------------------------|---------|---------|---------|---------|
| KF | 0.74 | 0.46 | 0.35 | 0.15 |
| KF-9.5HT30 | 0.54 | 0.21 | 0.23 | 0.42 |
| KF-8AN20 | 1.16 | 0.86 | 1.95 | 0.23 |
| KF-8AN20-8ST30 | 0.69 | 0.58 | 1.05 | 0.21 |
| KF-8AN20-8ST30-9.5HT30 | 0.51 | 0.45 | 1.08 | 0.17 |
| KF-8AN20-9.5HT30-8ST30 | 0.52 | 0.38 | 1.04 | 0.16 |

important role in the adsorption of nitrate anion. Based on our previous study, surface acidic oxygen function such as carboxy groups (–COOH) strongly inhibits the adsorption of nitrate anion [17]. But in this study, such strong acidic groups were not present, because all adsorbents had been experienced heating atmospheres above 800 °C in which carboxy groups were completely removed as CO/CO₂ by decomposition and/or converted to neutral carbonyl groups on the carbon surface [21]. In contrast to carboxy groups, aliphatic amine such as benzyl and phenethyl groups can accept protons (H⁺) to be positively charged and becomes preferable adsorption sites of nitrate [22]. In this case, the aliphatic amine will also be decomposed by heating below 800 °C.

To the best of our knowledge based on our experience for 15 years of experiments and the literature survey, two major adsorption sites of (a) π -electrons on graphene sheet without electron-withdrawing groups such as acidic functions [17] and (b) quaternary nitrogen (N-Q) can be principally operative as adsorption sites on carbonaceous adsorbents [11]. Since π -electron-rich graphene sheet exhibits weakly negative-charged surface, the graphene

can accommodate protons (H⁺), and then the surface can attract nitrate anion as well. Quaternary nitrogen (N-Q) is always positively charged on the graphene surface independent of solution pH and then it is an ideal sites to adsorb nitrate anion, whereas pyridinic nitrogen (N-6, pKa ranging 5–6) and pyrrolic nitrogen (N-5) may attract nitrate only in acidic region accommodating protons (H⁺) [23]. In contrast, repulsive force may be operative between these N-6 and N-5 species and nitrate in neutral and basic region, because nitrogen elements of N-6 and N-5 have slightly negative charge due to the lone-pair electrons of nitrogen releasing protons (H⁺). From the viewpoints of the π -electron-rich graphene sheet and the quaternary nitrogen (N-Q), adsorption amounts of nitrate on BAC, KF, KF-9.5HT30 and KF-8ST30 can be interpreted in terms of specific surface area rather than quaternary nitrogen (N-Q), whereas a small amount of N-Q seems to be detected on the surface of KF and KF-9.5HT30 as shown in Table 3 and Fig. 2. For nitrate adsorption amounts, KF is better than BAC due to the increase in specific surface area and amount of N-Q, whereas in spite of an opposite correlation with specific surface area, KF-9.5HT30 is greater than KF, possibly caused by the decrease in adsorption inhibitors of N-5 and N-6 for KF-9.5HT30. For the KF series treated with acetonitrile thermal CVD, N-Q as well as π -electron-rich graphene sheet seems to play a decisive role for the adsorption of nitrate anion. A 30 mL of acetonitrile thermal CVD for 2 grams of KF almost completely plugged pore structure of KF. Even though more than 99% specific surface area was lost for KF-8AN30, surprisingly adsorption amount of nitrate still remained 74% of KF. This could be caused by the largest amount of N-Q (1.95%) that should compensate the drastic loss

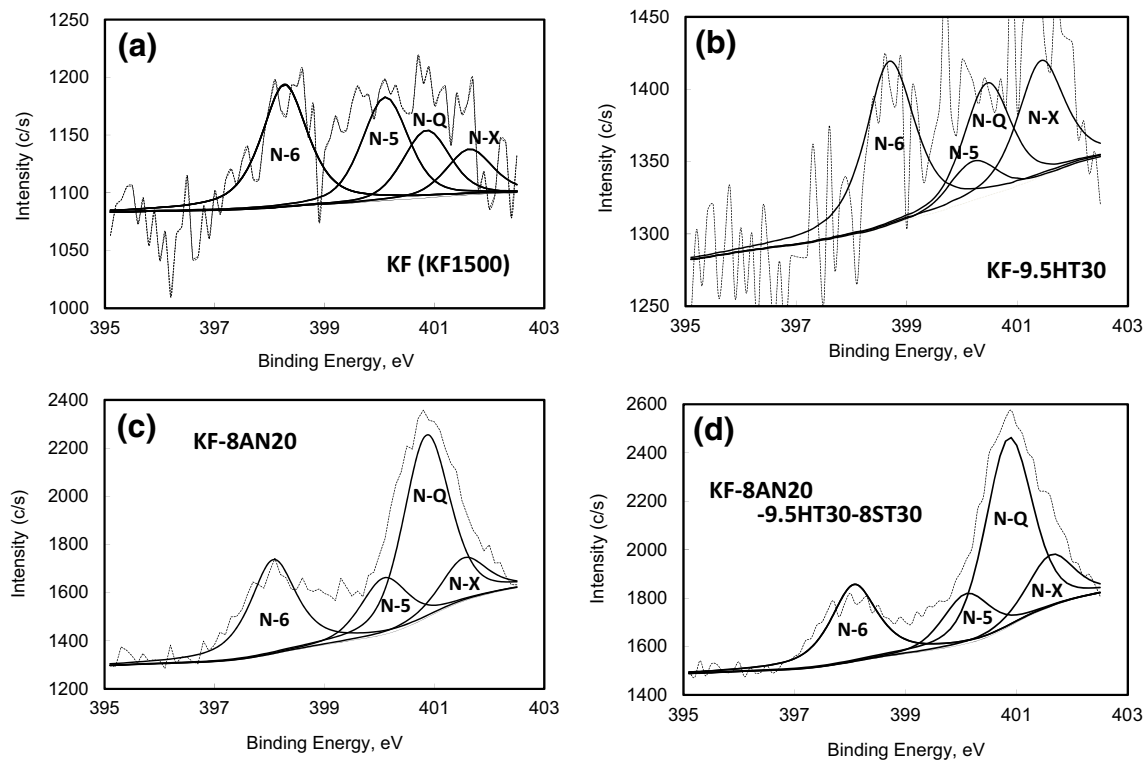


Fig. 2 N(1s) XPS spectra of modified KF1500 activated carbon fibers (ACFs)

of BET specific surface area from 1540 down to 10 m²/g. Fortunately, steam activation of KF-8AN30 with 30 mL pure water again led to the great recovery of the specific surface area from 10 up to 1190 m²/g, whereas nitrogen content and N-Q species moderately decreased from 4.2 to 2.5% and from 1.95 to 1.04%, respectively. Probably by increasing specific surface area accompanied by increasing the extent of exposure of N-Q inside the pore structure, adsorption amount of nitrate anion was raised from 0.28 to 0.61 mmol/g for KF-8AN20-8ST30, even greater than 0.38 mmol/g of the original KF. The further annealing at 950 °C of KF-8AN20-8ST30 resulted in slight decrease in adsorption amount of nitrate anion, despite slight increase in specific surface area and constant values of nitrogen content and N-Q percentage. We are not sure, but due to decrease in oxygen content from 14.1 to 8.8% (declined by 40%), the additional 9.5HT30 annealing, KF-8AN20-8ST30-9.5HT30, may enhance loss of some specific oxygen function as lactone group which can be slightly positively charged and become preferable adsorption site for nitrate. A different sequential modified order of KF-8AN20-9.5HT30-8ST30 showed the greatest adsorption amount of nitrate anion (0.71 mmol/g). After acetonitrile thermal CVD, 9.5HT treatment could efficiently convert doped nitrogen into N-Q inside the plugged structure, and the subsequent steam activation would develop

pore structure as large as 1560 m²/g keeping preferable nitrogen, principally N-Q, and oxygen species on KF structure. Since BET surface area of KF-8AN20-9.5HT30-8ST30 is as great as the original KF despite the enhancement of adsorption capacity of nitrate, surface chemistry should be significantly altered to enhance the adsorption capacity of nitrate, especially due to the increase in positively charged N-Q. On the assumption that only the increase in N-Q should contribute to the enhancement of nitrate adsorption, since N-Q was increased by 0.69% ($\Delta 0.49$ mmol/g) from 0.35% (0.25 mmol/g) in KF to 1.04% (0.74 mmol/g) in KF-8AN20-9.5HT30-8ST30, and the adsorption amount of nitrate was increased by $\Delta 0.33$ mmol/g from 0.38 mmol/g for KF to 0.71 mmol/g for KF-8AN20-9.5HT30-8ST30, about 70% ($\Delta 0.33$ mmol/g divided by $\Delta 0.49$ mmol/g) of newly introduced N-Q could become adsorption sites for nitrate from a mathematical point of view. For the second best treatment of KF-9.5HT30-8AN20-9.5HT30-8ST30, specific surface area was also the second largest among the 10 adsorbents, but nitrogen could not be effectively doped into KF; total nitrogen content was 1.8%, close to the original KF (1.7%). Doping of carbon using n-heptane instead of acetonitrile, KF-8(C7)15-9.5HT-8ST30, as a reference material, in which both nitrogen and oxygen were decreased compared to the original KF, exhibited the largest nitrate adsorption amount among the adsorbents without

additional nitrogen doping, but less than any activated nitrogen-doped adsorbent using the acetonitrile CVD.

4 Conclusions

Rayon (cellulose)-based KF1500 activated carbon fiber (ACF) was modified with acetonitrile thermal CVD at 800 °C combined with steam activation at 800 °C and/or annealing at 950 °C to prepare adsorbents for removal of nitrate (NO_3^-) from aqueous phase. Sequential treatment of KF1500 with acetonitrile thermal CVD, annealing at 950 °C and then steam activation (KF-8AN20-9.5HT30-8ST30) exhibited the greatest adsorption capacities of 0.71 mmol/g, nearly 2 times greater than the original ACF. Since there is no major difference between KF and KF-8AN20-9.5HT30-8ST30 in specific surface area, the increase in quaternary nitrogen (N-Q) from 0.35 to 1.04% by the thermal CVD and the annealing could play a decisive role in the enhancement of nitrate adsorption. Consequently, nitrogen doping, particularly quaternary nitrogen (N-Q), onto carbon surface could be supposed to be one of the most effective strategies for increasing adsorption capacity of anionic pollutants in aquatic phase.

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Compliance with ethical standards

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

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