Adsorptive Removal of Nitrate from Aqueous Phase Using Steam Activated and Thermal Treated Polyacrylonitrile (PAN) Fiber

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Abstract: Approximately three grams of black colored air-stabilized polyacrylonitrile (PAN) fiber, namely PYROMEX (PYR), containing nitrogen element was activated by steam at 800°C to develop porosity and thermally treated at 900-1000°C in helium to convert a part of nitrogen species to quaternary nitrogen (N-Q) using various combinations of the steam and thermal treatments in a 25 φ inner diameter quartz tube, and adsorption capacity of nitrate anion from aqueous solution was measured. Steam activation at 800°C by 20 mL water charge and consecutive heat treatment at 950°C for 30 min (PYR-8ST20-9.5HT30) showed the largest nitrate adsorption capacity of 0.64 mmol/g among all prepared adsorbents. Effect of solution pH on nitrate adsorption was also investigated at the initial nitrate concentrations of 0.85-5.06 mmol/L for PYR-8ST20-9.5HT30 compared with thermal treated cellulose based ACF at 950°C for 30 min (KF1500-9.5HT30). The adsorption amount of nitrate on PYR-8ST20-9.5HT30 was always greater than that on KF1500-9.5HT30 at any condition examined in the experiments in spite of specific surface area of PYR-8ST20-9.5HT30 being less than half of KF1500-9.5HT30. Langmuir type adsorption isotherms of nitrate could be applied at pH range from 3 to 6. Maximum adsorption capacities of PYR-8ST20-9.5HT30 and KF1500-9.5HT30 calculated from the isotherms were 0.56-0.72 and 0.50-0.61 mmol/g, respectively, altering the values depending on the solution pH. The higher adsorption capacities could come from the greater amount of nitrogen, particularly quaternary nitrogen (N-Q), and the less oxygen that would work as inhibitor sites for nitrate adsorption, on PYR-8ST20-9.5HT30 than KF1500-9.5HT30.

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1. Introduction

Contamination of nitrate in ground water and surface water has been one of the most widely known environmental problems worldwide [1]. In India nitrate concentrations in open wells were reported from 25 to 140 mg/L at Jhunjhunu district located at the west of New Deli [2], and also ranging from 8 to 213 mg/L in the ground water samples of Sawai Madhopur at the south of New Deli [3]. Likewise in United States, nitrate contamination was reported to spread nationwide, in which more than 300 mg/L NO₃⁻ was observed from the public supply wells in an agriculture area at York in Nebraska [4]. A lot of methods have been examined to reduce nitrate levels in ground water, for instance, ion exchange process, reverse osmosis, chemical denitrification, electrodialysis, electrocatalytic reduction, biological denitrification, heterotrophic denitrification, bioreactor and combination of them [5, 6]. Among these methods, adsorptive removal including ion exchange process is an attractive from an economical point of view [7]. There have been lots of adsorbents to be examined to remove nitrate from water. They are activated carbon cloth, carbon nanotube, graphene sheet, sepiolite, red mud, mesoporous silica, zeolite and their surface modified materials by metal oxides impregnation and amine-grafting [8, 9].

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Activated carbons are also applied for the reduction of nitrate level in water, for example, using surface modification with urea [10] and ammonia [11]. Carbonaceous adsorbents have advantages compared to other adsorbents in high robustness against thermal and acid-base treatments that are frequently utilized for regeneration of adsorbents. Carbon-based adsorbents were also prepared from nitrogen rich melamine sponge in our previous study and then further treated with methyl iodide to convert nitrogen species on the carbon surface to positively charged quaternary nitrogen (N-Q) to enhance nitrate adsorption [12]. In the present study, nitrogen rich polyacrylonitrile (PAN) fiber was used to prepare new activated carbon fibers (ACFs) as adsorbents for the nitrate anion (NO$_3^-$) removal.

2. Experimental

2.1 Preparation of adsorbents

The starting material of polyacrylonitrile (PAN) based carbon fiber was oxidized PAN fiber felt, namely PYROMEX, purchased from Toho Tenax Co., Ltd., Japan. PYROMEX, hereafter referred to as PYR, was produced from white colored polyacrylonitrile fiber; air treatment between 200°C (preferably 250°C) and 300°C was carefully conducted to form and stabilize so called rudder structure of resultant black colored PAN carbon fiber [13]. A mass of approximately 3 grams of PYR felt was put into a quartz tube of 25 φ inner diameter and quartz wool was also placed next to PYR or KF1500 at upper stream side in the tube for the purpose of sufficiently heating up steam or helium flow up to desired temperature before contacting the gases to PYR or KF1500. At first steam was introduced at 800°C to the quartz tube by injecting 10-30 mL of water to expand the surface area of PYR and then activated PYR was heat treated in helium flow at 900-1000°C. The reverse order of the steam activation and heat treatment was investigated as well. When PYR was treated by steam using the injection of 20 mL water at 800°C followed by treated in helium flow at 100 mL/min at 950°C for 30 minutes, the sample was designated as PYR-8ST 20-9.5HT30. Thereby, PYR-8ST30-9.5HT120 stands for 800°C steam activated with 30 mL water charge for 3 g PYR for the first step and heat treated at 950°C for 120 minutes for the second step.

As reference materials, heat treatment at 950°C for 30 minutes of cellulose based activated carbon fiber, namely KF1500 LDA, purchased from Toyobo Co., Ltd., Japan, and commercially available bead shaped granular activated carbon, L-BAC LP, which was supplied from Kureha Corporation, Japan, and free from ash and acidic oxygen functional groups, was used as received. The two reference adsorbents are designated as KF1500-9.5OG30 and GAC, respectively.

2.2 Characterization of carbon adsorbents

Morphology of the adsorbents was observed with scanning electron microscope (SEM, JEOL JSM-6510). Textural and surface properties of the carbon adsorbents used in the experiments were characterized by N$_2$ adsorption and desorption isotherms at -196°C using BELSORP-mini II (MicrotracBEL Corp., Japan) surface area analyzer. The specific surface area was calculated by B.E.T. and SPE methods using $a$ plots [14]. Total pore volume ($V_{\text{total}}$) was obtained from $N_2$ volume absorbed at relative pressure ($p/p_0$) at 0.995. Micropore volume ($V_{\text{mic}}$) was from $a$ plots in SPE methods and then mesopore volume ($V_{\text{mes}}$) was calculated from difference between $V_{\text{total}}$ and $V_{\text{mic}}$. The pH of the point of zero charge of the adsorbents ($pH_{\text{zc}}$) was also determined with pH drift method using 1 M HCl or 1 M NaOH solution; the equilibrium pH was plotted against the initial pH using pH range from 2 to 9 and pH$_{\text{zc}}$ was defined by the point when the initial pH was equal to the equilibrium pH [15]. Elemental content of carbon, hydrogen and nitrogen (CHN) was measured by elemental analyzer (Perkin-Elmer, PE 2400 II). The other elements were assumed to be oxygen. The amount of surface nitrogen species were determined using X-ray photoelectron spectroscopy (XPS, PHI 1800, ULVAC-PHI).

2.3 Adsorption experiments of nitrate

Thirty milligrams of each prepared adsorbent were measured and dosed into 15 mL of sodium nitrate (NaNO$_3$) solution in the 30 mL capped flask. The solution was agitated for at least 12 hours, because we had already confirmed that adsorption equilibrium attained within 6 hours in the previous kinetic study. Screening test for prepared sample was conducted using the initial nitrate concentration of 323 mmol/L, for which the initial solution pH was adjusted to about 3 adding 1 M HCl solution. As mentioned in the latter section, PYR-8ST20-9.5HT30 exhibited highest adsorption capacity in all prepared adsorbents in the study. The cellulose based KF1500 treated at 950°C for 30 min (KF1500-9.5HT30) was also...
used as a reference adsorbent in order to be compared with PYR-8ST20-9.5HT30. For the two adsorbents, further study was carried out; influence of equilibrium solution pH (pHₕ) on the amount of nitrate adsorption was measured, and then adsorption isotherms were drawn at pHₕ 3.0, 4.5 and 6.0 and Langmuir adsorption model was applied as a theoretical isotherm to calculate the adsorption affinities and capacities of nitrate ion onto the two adsorbents.

3. Results and discussion

3.1 Screening test of prepared adsorbents

Fig. 1 shows some screening results to select the optimum adsorbent for uptaking nitrate from aqueous phase picked up among more than 300 prepared samples by trial and error. The reproducibility of the experimental data is considered to be good, since the coefficient of variation (C.) for the preparation of adsorbents and then adsorption experiments of nitrate have been controlled by less than 3% in our preliminary study and in the current experiments as well. GAC, a bead shaped granular activated carbon, could accommodate nitrate ion only by 0.25 mmol/g. The other reference material, an activated carbon fiber of KF1500-9.5HT30, exhibited a better adsorption amount of nitrate by 0.52 mmol/g that was twice greater than GAC. The large difference could come from 4 times greater nitrogen content as can be seen in Table 1, particularly greater amount of quaternary nitrogen (N-Q) configuration of KF1500-9.5HT30 than that of GAC as described in detail in the latter section, whereas there was only acidic oxygen free π-electron rich surface of graphene sheets in GAC which was confirmed to be adsorption site for nitrate by accommodating some amount of protons (H⁺) rather than Na⁺ from aqueous phase to form slightly positively charged sites [16]. Here quaternary nitrogen (N-Q) in graphene sheet is always positively charged on the carbon surface, hence N-Q can always attract anionic nitrate ion independent of solution pH, whereas other nitrogen configurations were necessarily affected by solution pH in aqueous phase altering positively or negatively charged N-species depending on pKₐ varying with nitrogen configurations, for example, sp² or sp³ of nitrogen hybridization [17].

As for PYR series, PYR-8ST10 that could adsorb nitrate by 0.54 mmol/g is an adsorbent as well as KF1500-9.5HT30. However, PYRs first treated with 950°C followed by steam treatments at 800°C (PYR-9HT30-8ST10 and PYR-9.5HT60-8ST30) adsorbed similar or less amount of nitrate than PYR treated with steam only (PYR-8ST10). Heat treatment at 900-1000°C for 30 minutes after steam treatment at 800°C using 10 mL water charge (PYR-8ST10-9HT30, -9.5HT30 and -10HT30) represented similar or less

**Table 1** Properties of PAN-based activated carbon fiber (ACF), cellulosed-based ACF and granular AC

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sample mass</th>
<th>% Soret</th>
<th>Specific surface area (m²/g)</th>
<th>Biodegradation (%)</th>
<th>N-Q (%)</th>
<th>N-Q (%)</th>
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<th>N-Q (%)</th>
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<tr>
<td>KF1000-9.5HT30</td>
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<tr>
<td>GAC</td>
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* Calculated by difference.

Fig. 1 Amounts of nitrate adsorption onto various activated carbon fibers (ACFs) prepared from polyacrylonitrile (PAN) fiber, granular activated carbons (GAC) and cellulosed based ACF (KF1500-9.5HT30) as reference adsorbents. Thirty milligrams of adsorbent dosage into 15 mL nitrate solution at pH 3.0 and the initial concentration of 3.23 mmol/L. The equilibrium pH (pHₕ) was measured after at least 12 hours agitation at room temperature.
adsorption capacities than the only steam treatment (PYR-8ST10). Decrease in adsorption amount could be estimated that the carbon structure of PYR might shrink accompanied by decrease in surface area and/or decrease in effective nitrogen species at the higher temperatures of 900-1000°C.

On the other hand, deeper steam activation using water charge of 20 and 30 mL as PYR-8ST20 and PYR-8ST30, respectively, followed by the high temperature treatment (9.5HT30) resulted in further improvement of nitrate adsorption of 0.60-0.64 mmol/g compared with the steam activation only (PYR-8ST10 and -8ST20). The enhancement could be caused by the significant decrease in oxygen content that could be inhibitor of nitrate adsorption in contrast to nitrogen species [16]. But the adsorption amount of nitrate varied with period of heat treatment at 950°C. In PYR-8ST30-9.5 HTx series in which x is holding time in min, x value of 30 (PYR-8ST30-9.5HT30) could uptake greater amount of nitrate than the other x values of 0, 60 or 120, indicating an optimum period should be present around 30 minutes for heat treatment at 950°C. Pels et al. studied the nitrogen configurations of nitrogen-containing carbonization materials from carbazole, acridine and polycrylonitrile (PAN) with XPS analysis, and demonstrated that quaternary nitrogen (N-Q) was increased during pyrolysis at 800-1000°C by converting pyridinic N (N-6) to N-Q, in which higher temperature was more preferable for the N-Q formation [18]. Li et al. also observed that N-Q was increased by annealing temperature above 900°C for NH3 treatment of graphene oxide [19], because nitrogen also could be doped inside the graphite structure during the NH3 treatments. Consequently the holding time of 30 minutes in the 950°C heat treatment might maximize surface N-Q after 800°C steam activation of PYR. Shorter holding time could lead to an insufficient conversion of N-6 to N-Q, but longer holding time more than 60 minutes as well as higher temperature might shrink the structure and/or reduce the nitrogen content itself; the shrunken structure could decrease surface area resulting in the reduction of the number of nitrogen species exposed to the surface accompanied by the reduction of total nitrogen content.

3.2 Morphology and properties of adsorbents

Two prepared adsorbents of PAN based ACF (PYR-8ST20-9.5HT30, 20% yield on PYR) and cellulose based ACF (KF1500-9.5HT30, 87% yield on KF1500 LDA) as a reference adsorbent were employed to inspect influence of solution pH on uptaking nitrate ion from aqueous phase. Fig. 2 displays the SEM images of the adsorbents. Similar morphologies could be seen at these SEM magnifications, although slight differences can be observed in shape and thickness between the fibers. Textural and chemical properties of the adsorbents were compiled in Table 1. Specific surface area and pore volume of KF1500-9.5HT30 were twice as large as those of PYR-8ST20-9.5OG30. In contrast, nitrogen composition and content of nitrogen configurations of KF1500-9.5HT30 were approximately 0.3-0.7 of those of PYR-8ST20-9.5HT30. There were no significant differences between the ACF adsorbents in the pH of the point of zero charge (pHpz) and the elemental composition of carbon, hydrogen and oxygen. The nitrogen configurations mentioned above were calculated from composition of nitrogen species observed with the XPS analysis assuming pyridinic nitrogen (N-6) of binding energies 398.6 ± 0.3 eV, pyrrolic nitrogen (N-5) of 400.5 ± 0.3 eV, quaternary nitrogen (N-Q) of 401.3 ± 0.3 eV and mixture of pyridine-N-oxide, pyridone, etc. (N-X) of binding energies 402-405 eV were present as shown in Fig. 3 on accordance with the deconvolution proposed by Pels et al.[18].

3.3 Influence of equilibrium solution pH on nitrate adsorption

Fig. 4 represents the influence of equilibrium solution pH (pHs) on adsorption amount of nitrate onto the ACF adsorbents. In all initial nitrate concentrations ranging from 0.85 to 5.06 mmol/L examined, adsorption amounts of nitrate on PYR-
the solution pH. Similar results could be obtained in our previous study on nitrogen doped granular activated carbon at the low initial nitrate concentration of 0.81 mmol/L; adsorption of nitrate was also declined at lower pH and the restriction was supposed to be caused by competitive adsorption with chloride anion [11], whereas such a restriction was never observed at higher initial concentrations of nitrate as well [20].

3.4 Adsorption isotherms

Using the approximate solid lines in Fig. 4, adsorption isotherms were plotted at equilibrium solution pH (pH) 3.0, 4.5 and 6.0 as displayed in Fig. 5. The solid lines were drawn assuming following Langmuir model (Eq. 1) using the Langmuir parameters obtained from Eq. 2 with good correlation coefficients, that was linear form of Eq. 1, as can be seen in Table 2, where Qc and Xn are equilibrium and maximum adsorption amounts in mmol/g. and K and C are adsorption affinity in L/mmol and equilibrium nitrate concentration in mmol/L, respectively.

\[
Q_c = \frac{K_c C}{1 + K_c X_{n}} \quad \text{Eq. 1}
\]

\[
C = \frac{1}{X_{n}} C_c + \frac{1}{K_c X_{n}} \quad \text{Eq. 2}
\]

Comparing these parameters, adsorption

8ST20-9.5HT30 were always greater than those on KF1500-9.5HT30. Except the initial nitrate concentration of 0.85 mmol/L, the lower the solution pH values, the greater the adsorption amounts for the other higher initial nitrate concentration due to the increase of surface proton (H+) concentration on the adsorbents at lower pH, that attract negatively charged nitrate in aqueous phase. However, in case of the initial nitrate concentration of 0.85 mmol/L, adsorption amount of nitrate was restricted when pH decreased less than 4 as obviously seen in Fig. 4 (A). The restriction of the nitrate adsorption can be explained by increasing co-existing chloride ions coming from hydrochloric acid that is added to reduce

![Fig. 3](image1.png)

**Fig. 3** The nitrogen configurations (N1s) of PYR-8ST20, PYR-8ST20-9.5HT30 and KF1500-9.5HT30 by the XPS analysis (PHI 1800, ULVAC-PHI) assuming pyridinic nitrogen (N-6), pyrrolic nitrogen (N-5), quaternary nitrogen (N-Q) and mixture of pyridine-N-oxide, pyridone and some unidentified nitroten species (N-X) are present on accordance with the deconvolution by Pels et al. [18].

![Fig. 4](image2.png)

**Fig. 4** Influence of equilibrium solution pH (pH) on the amount of nitrate adsorption at the initial nitrate concentrations of (A) 0.85 mmol/L, (B) 1.65 mmol/L, (C) 3.26 mmol/L and (D) 5.06 mmol/L. Adsorption conditions; the same as described in Fig. 1. Black circles; PYR-8ST20-9.5HT30, black triangles; KF1500-9.5HT30, solid lines; approximate lines.
The affinities of PYR-8ST20-9.5HT30 is a little weaker than KF1500-9.5HT30 at pH 3.0, but when pH 4.5 the reversal of affinity order was observed, and then at pH 6.0, the $K_r$ value of PYR-8ST20-9.5HT30 is three times larger than that of KF1500-9.5HT30. Likewise the $X_{max}$ values of PYR-8ST20-9.5HT30 ranged from 0.56 to 0.70 mmol/g, whereas ranging from 0.50 to 0.61 mmol/g for KF1500-9.5HT30. From the practical points of view, high performance adsorption should be made at lower concentration of nitrate. PYR-8ST20-9.5HT30 was always superior to KF1500-9.5HT30 in all pH ranges; as easily implied from Fig. 5, the gap between the two adsorbents widened as pH value went up from 3.0 via 4.5 up to 6.0. The data analysis of the adsorption isotherms of nitrate reveals that PYR-8ST20-9.5HT30 has an advantage to be used in aqueous solution of weak acidic and neutral conditions ranging from pH 4.5 to 6.0. The higher performance of PAN-based ACF can be attributed to nitrogen species, particularly to quaternary nitrogen (N-Q) configuration for the present, because about 2 times large amount of nitrogen was contained in PYR-8ST20-9.5HT30 compared to KF1500-9.5HT30 (Table 1), even though the other chemical properties show no significant differences and textural properties such as surface area and pore volume of PYR-8ST20-9.5HT30 are even two times smaller than those of KF1500-9.5HT30. The N-Q content of PYR-8ST20-9.5HT30 was also 1.8 times greater than KF1500-9.5HT30 and the other configurations of N-6, N-5 and N-X configurations can have contribution for nitrate adsorption to some extent as well. In general N-6, N-5 and N-X nitrogen configurations have some pK_r value ranging from 3 to 10 [17], in which pH value less than pK_r exhibits positively charged species that attract nitrate ion, whereas in principle N-Q configuration can be constantly present as positively charged adsorption sites at any solution pH, advantageous for the adsorption of anionic pollutants. Contribution of N-Q configuration in nitrate adsorption was also reported for N-Q function grafted mesoporous silica adsorbent, in which adsorption amount of 0.63 mmol/g was achieved [11].

### 4. Conclusion

Nitrogen-containing polyacrylonitrile (PAN) based activated carbon fibers (ACFs) were prepared from commercially available thermally stabilized PAN fiber (PYROMEX) using steam activation at 800°C and heat treatment at 900-1000°C by trial and error to develop ACFs to remove nitrate by adsorption from aqueous phase. An 800°C steam activation and consecutive 950°C heat treatment of PYROMEX...
yielded ACF adsorbent of 710 m²/g with the maximum adsorption capacity of 0.7 mmol/g. Reference material of cellulose based ACF containing less amount of nitrogen species achieved 0.6 mmol/g. This should be caused by not only nitrogen species, but also higher specific surface area of 1530 m²/g of the cellulose ACF. Based on the analysis of adsorption experiments and characterization of the adsorbents, nitrogen species in PAN-ACF can play an important role for the enhancement of nitrate adsorption. On the contrary, oxygen species could affect negative effect on the nitrate adsorption. Within all nitrogen configurations, greater amount of quaternary nitrogen (N-Q) observed in PAN-ACF could particularly participate in the nitrate adsorption.

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