Note

Adsorptive Removal of Nitrate from Water Using Modified Activated Carbon Fibers

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Abstract

Activated carbon fiber (ACF) from cellulose based ACF (KF1500) was modified to give anion ion exchange functionality using three sequential modification methods; acetonitrile thermal chemical vapor deposition (CVD) at 800°C, heat treatment at 950°C and then steam activation at 800°C for the purpose of maximizing ion exchange capacity of nitrate (NO_3^-). The maximum adsorption amount of 0.71 mmol/g was achieved, which was 1.9 times larger than non-modified original KF1500 (0.38 mmol/g) but a half the amount of ion exchange resin of HP555 (1.4 mmol/g), under the same experimental conditions.

Keywords: Ion exchange, Activated carbon fiber, Adsorption of nitrate, Nitrogen doping, Acetonitrile thermal CVD

1. Introduction

Globally widespread contamination problems in air, land and water have already been attracted attention in this half a century. However, the situations are still going worse in developing countries, although strict environmental regulations have been introduced in developed countries. In this study, development of carbonaceous adsorbents is carried out to efficiently remove ionic pollutants from water in order to contribute to the conservation of water environment. Adsorptive removal of ionic pollutants is generally progressed via ion-exchange mechanism. For cation exchange resins, Na^+ is released to aqueous phase when cationic heavy metal ions such as Pb^{2+} , Cd^{2+} and Cs^+ adsorb to the resins, while Cl^- is discharged into water in case of the adsorption of anionic contaminants like NO_3^- , F^- and H_2PO_4^- . In general, carbonaceous adsorbents, typically activated carbon (AC) and activated carbon fiber (ACF), have been employed to uptake non-ionic organic pollutants using the hydrophobic interaction between the organic contaminants and graphene surfaces of AC and ACF¹⁾. In contrast, for the removal of ionic pollutants, hydrophilic surface is required whether they are cationic or

anionic contaminants. Ceramic adsorbents such as zeolites and shells are good for both cationic and anionic pollutants, because there are electron rich and deficient sites simultaneously on the ceramic surfaces. As for ion exchange resins, carboxy and sulfonic functions are operative for cation adsorption, while quaternary nitrogen (N-Q) contributes to anion adsorption. Although the ceramic and resin adsorbents are widely used for both laboratory and commercial scales, acidic and basic conditions are not preferable for ceramics and heat treatment should be avoided for ion exchange resins. As mentioned above, carbonaceous materials, ceramics and ion exchange resins have advantages and disadvantages each other.

In this study, we have tried to develop new ACFs to capture ionic pollutants on the graphene surface of them by various modifications of carbon surfaces, because carbonaceous materials are tolerant of acid/base solution and heating stress. Suitable surface of ACs and ACFs for attracting cationic contaminants could have been successfully prepared by the oxidation of carbon surfaces using several oxidants like concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$ system²⁾ and aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ³⁾. For the present, we are trying to modify the

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carbon surfaces suitable for removing anionic pollutants. Graphene surfaces themselves are good for the adsorption of anionic pollutants only in the acidic region, because a slightly negatively charged graphene sheet originated from π -electrons of condensed benzene rings can accommodate protons forming a positively charged carbon surface ⁴⁾. But the electron density on the graphene sheets is easily lowered by acidic oxygen functional groups remained on the peripherals of the graphite structures, thereby removing oxygen from graphene sheets by reduction is a good option to increase the adsorption amounts of anionic contaminants ⁵⁾. However, the surface charges of graphene sheets are also altered by solution pH. Introduction of specific nitrogen functionalities is another option to enhance the adsorption amount of anions. The quaternary nitrogen (N-Q) at peripheral and/or inside the graphene structures always positively charged, hence the attractive force toward anionic contaminants is working independent of solution pH ⁶⁾. Aliphatic amines of pK_a values more than 9-10 are protonated ($-NH_3^+$) in the range from acidic to pH 9-10 ⁷⁾ becoming suitable sites for anionic contaminants as well. Both quaternary nitrogen (N-Q) and aliphatic amine on the adsorbents have been proven to be effective for the adsorption of anions ⁸⁾.

In the present study, surface reduction of activated carbon fibers (ACFs) and nitrogen doping on the graphite structure of ACFs were examined; surface reduction was carried out to maximize the π -electron density of graphene sheets and nitrogen doping was conducted in order to increase the quaternary nitrogen (N-Q) in the graphite structure. The evaluation of the prepared carbonaceous adsorbents was performed by the adsorptive removal of nitrate (NO_3^-) from aqueous solution.

2. Experimental

Activated carbon fiber (ACF) KF1500 LDA, hereafter denoted as KF, used in the study is purchased from Toyobo Co., Ltd., Japan. KF is produced from cellulosic fiber in an industrial scale. KF was dried in an oven at 110°C for 30 min before use, weighed (0.7-0.9 g) and placed in 30 ϕ quartz tube and heated up to desired temperature between 800 and 950°C with a horizontal cylindrical furnace to modify the graphene surface of KF. All heat treatments of KF were conducted under helium flow at 50 mL/min. Based on our preliminary study of preparation of more than 200 different modified samples (not shown here), three methods and their combinations were employed for the heat-treated modification; thermal chemical vapor deposition (CVD) by 20 mL charge of acetonitrile at 800°C for doping nitrogen onto KF surface (8AN20) ⁹⁾, steam activation by 30 mL water charge at 800°C for developing pore structure of KF (8ST30), and just heating at 950°C, holding time of 30 min, for converting a part of doped nitrogen to quaternary nitrogen (N-Q) species (9.5HT30) ¹⁰⁾. Sample name of KF-8AN20-8ST30-9.5HT, for instance, means KF (KF1500) was

heat-treated with all above modification methods in the order of thermal CVD, steam activation and then just heat-treatment. For comparison with acetonitrile treatment, n-heptane (15 mL) thermal CVD was conducted in addition, instead of the acetonitrile (20 mL) CVD, referred to as KF-8(C7)15-9.5HT30-8ST30. All prepared ACFs were evaluated by nitrate adsorption amount at pH around 3. Thirty milligrams of each modified KF samples was put into Erlenmeyer flask containing 15 mL of sodium nitrate ($NaNO_3$) solution. The starting solution pH and the initial concentration of nitrate were respectively about 3 and 200 mg (NO_3^-)/L (3.23 mmol/L). The mixture was stirring for at least 12 hours at ambient temperature and equilibrium solution pH was adjusted between 2.8 and 3.5, most of the case pH 3.0-3.5. The initial and the equilibrium concentrations of nitrate were measured by an Ion Chromatography (Nippon Dionex KK, model ICS-1100). The adsorption amount in mmol/g at equilibrium was calculated from the difference in concentrations and sample weight of 30 mg.

3. Results and Discussion

Fig. 1 shows the equilibrium adsorption amounts of pristine and various prepared adsorbents and the adsorption amounts of nitrate (NO_3^-) were varied from 0.25 to 0.71 mmol/g in which all adsorption was assumed to be progressed via ion exchange mechanism, because in our previous study, discharge of Cl^- from the adsorbent into the solution by exchanging with NO_3^- was observed in all investigated similar carbonaceous anion ion-

Fig. 1 Adsorption amount of NO_3^- (Q_e in mmol/g) onto various carbonaceous ion-exchangers in aqueous solution. Black circle ($\bullet$); equilibrium solution pH (pH_e).

Table 1 Properties of activated carbon (BAC) and activated carbon fiber (KF)

Sample name	Textual and surface properties		
	S_{BET}	Pore volume,	Pore diameter,
	m^2/g	cm^3/g	nm
KF	1560	0.70	0.74
BAC	1380	0.60	0.57

Sample name	Bulk elemental composition			
	Carbon, %	Hydrogen, %	Nitrogen, %	Oxygen*, %
KF	88.4	0.6	1.7	9.3
BAC	94.0	0.7	0.4	5.0

*calculated by difference

exchangers ¹¹⁾. The adsorption amount on ion exchange resin of HP555 as a reference adsorbent was 1.4 mmol/g, which was twice as large as the maximum adsorption amount of 0.71 mmol/g. BAC (bead-shaped activated carbon) purchased from Kureha Corporation is also a reference material. Adsorption amount of KF (0.38 mmol/g) was larger than that of BAC (0.25 mmol/g). As shown in **Table 1**, this is caused by higher surface area, higher pore volume, higher pore diameter and larger nitrogen content of KF than those of BAC, in spite of larger oxygen content of KF than BAC, in which acidic oxygen functional groups can inhibit the nitrate adsorption. Both KF-9.5HT30 (0.52 mmol/g) and KF-8ST30 (0.56 mmol/g) were better than KF, because oxygen reduction and further pore development from KF would be respectively achieved in KF-9.5HT30 and KF-8ST30. In contrast, nitrogen doping with acetonitrile thermal CVD on KF led to the significant decline in adsorption amount of nitrate (KF-8AN20, 0.28 mmol/g) compared to the original KF (0.38 mmol/g).

However, additional steam activation at 800°C resulted in remarkable enhancement of adsorption capacity (KF-8AN20-8ST30, 0.61 mmol/g) even more than KF-9.5HT30 and KF-8ST30. Thereby, the acetonitrile thermal CVD would plug the pore structure of KF, whereas effective nitrogen species could be introduced into the structure of KF and oxygen content would be decreased at the same time, and then nitrogen-containing pore structure could be achieved by the second activation by steam at 800°C (the first activation was done in the commercial production), in which nitrogen rich surface should be remained by selectively reducing carbon element during the pore development. Further heat-treatment of KF-8AN20-8ST30 at 950°C for the purpose of converting a part of doped nitrogen species into quaternary nitrogen (N-Q) could not successfully enhance the adsorption amount of nitrate (KF-8AN20-8ST30-9.5HT30, 0.57 mmol/g). This might be caused by shrunk pore structure and/or decrease in nitrogen content by

the 950°C heat-treatment. On the other hand, when the heat-treatment at 950°C was conducted just after KF-8AN20 and before 8ST30 treatment, the maximum adsorption amount could be observed in the study (KF-8AN20-9.5HT30-8ST30, 0.71 mmol/g), indicating that the order of treatments would play an important role to enhance the adsorption capacity. The heat-treatment at 950°C of KF-8AN20 might effectively convert doped nitrogen species inside the ACF into quaternary nitrogen (Q-N) without significant loss of nitrogen, after that steam activation at 800°C would develop pore structure with remaining effective nitrogen inside the structure. In case of the insertion of heat-treatment of KF at 950°C before 8AN20 treatment for KF-8AN20-9.5HT30-8ST30, a slight decline in adsorption amount was observed (KF-9.5HT30-8AN20-9.5HT30-8ST30, 0.65 mmol/g). The heat-treatment at 950°C of KF might shrink the pore structure of KF resulting in the slight decrease in the amount of nitrogen doping in the consecutive step. Furthermore, when n-heptane was used instead of acetonitrile for KF-8AN20-9.5HT30-8ST30 in the CVD treatment, as referred to as KF-8(C7)15-9.5HT30-8ST30, the adsorption amount was 0.58 mmol/g and the different amounts between 0.71 and 0.58 mmol/g could be respectively attributed to the presence and absence of effective nitrogen species; n-heptane could have decreased surface acidic oxygen by reduction but never increased nitrogen content. More detail characterization of the adsorbents will be required to elucidate the relationship between the properties of nitrogen doped ACF adsorbents and the adsorption amount of nitrate.

4. Summary

Activated carbon fiber (ACF) of KF1500 (KF) was modified using three heating methods under inert gas flow to prepare carbonaceous anion ion-exchanger. Sequential treatments of acetonitrile thermal CVD at 800°C, heat-treatment at 950°C and then steam activation at 800°C (KF-8AN20-9.5HT30-8ST30) led to maximize the adsorption amount of nitrate anion (0.71 mmol/g) in aqueous solution and the maximum amount was 1.9 times larger than that of the original KF (0.38 mmol/g) but still a half of ion exchange resin of HP555 (1.4 mmol/g).

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References

- 1) H. Tamon and M. Okazaki, *J. Colloid Interface Sci.*, **179**, 181 (1996).
- 2) K. M. Mena Aguilar, Y. Kose, Y. Amano, M. Machida and F. Imazeki, *J. Environ. Chem.*, **26**, 109 (2016).
- 3) M. Machida, S. Chensun, Y. Amano and F. Imazeki, *Bull. Chem. Soc. Jpn.*, **88**, 127 (2015).
- 4) M. Machida, T. Goto, Y. Amano and T. Iida, *Chem. Pharm. Bull.*, **64**, 1555 (2016).
- 5) K. Ota, Y. Amano, M. Aikawa and M. Machida, *Appl. Surf. Sci.*, **276**, 838 (2013).
- 6) T. Goto, Y. Amano and M. Machida, *TANSO*, **276**, 2 (2017).
- 7) J. H. Bitter, S. van Dommele and K. P. de Jong, *Catal. Today*, **150**, 61 (2010).
- 8) A. Dioum and S. Hamoudi, *J. Porous. Mater.*, **21**, 685 (2014).
- 9) Z. Yang, Y. Xia, X. Sun and R. Mokaya, *J. Phys. Chem. B*, **110**, 18424 (2006).
- 10) J. R. Pel, F. Kapteijn, J. A. Moulijn, Q. Zhu and K. M. Thomas, *Carbon*, **33**, 1641 (1995).
- 11) T. Goto, Y. Amano and M. Machida, *J. Chem. Eng. Jpn.*, **50**, 692 (2017).