

Application of titanate nanotubes for ammonium adsorptive removal from aqueous solutions



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ABSTRACT

The potential of adsorptive removal of ammonium with titanate nanotubes (TNT) was investigated. TNT was prepared via a hydrothermal treatment of TiO₂ powders in a 10 M NaOH solution at 150 °C for 24 h, and subsequently washed with HCl aqueous solution of different concentrations. Effects of the alteration of microstructures of TNT, induced by the acid washing process, on the ammonium removal performance were discussed. It was experimentally concluded that if the amount of Na⁺ in the TNT was not very low, TNT might be a good adsorbent for the removal of ammonium from aqueous solution with the adsorption capacity reaching 29 mg/g. The adsorption mechanisms of ammonium from aqueous solution onto TNT were examined with the aid of model analyses of adsorption equilibrium and kinetic data of ammonium.

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1. Introduction

Ammonium is the primary form of widespread nitrogen pollution encountered in wastewater and groundwater [1]. Although ammonium is a very important nutrient for algae, the excessive presence of ammonium not only leads to eutrophication in lakes, ponds, reservoirs, and coastal seas [2], but also increases the oxygen demand and exposes toxicity to aquatic life [3]. Moreover, it may also induce the corrosion/biological fouling problems in industrial water system due to the growth of algae blooms.

In recent years, an intensive effort to identify methods for the ammonium separation and removal from aqueous solutions was taken due to the increased awareness of the deleterious effects of ammonium. There are several methods for removing ammonium from aqueous solution, such as biological nitrification–denitrification [4], air-stripping [5], and ion-exchange [6]. Among the various methods, ion-exchange is more competitive over air-stripping and biological methods due to little influence at low temperature, relatively little space particularly its relative simplicity of application and operation, and environmentally friendly [7]. Ion-exchange,

therefore, seems to be an attractive method especially when low cost materials are used [8].

Kasuga et al. [9,10] recently reported the preparation of TiO₂-derived nanotubes by hydrothermal treatment of TiO₂ powders in a 10 M NaOH aqueous solution with different reaction temperatures and times. This method does not require any templates, and the prepared nanotubes have a small diameter of ca. 10 nm, and high crystallinity. Moreover, it is found that the microstructures of TNT are easily affected by the synthetic conditions, including such variables as reaction time, acid washing concentration, and calcination temperature [11–16]. Since the TNT derived from the hydrothermal method possesses ion-exchange properties [11,13,15–17] and is also characterized by a high specific surface area and pore volume [12], it may offer a special environment for the removal of ammonium through the cation exchange mechanism. Moreover, the above-mentioned hydrothermal method is also a simple, cost-effective, and environmentally friendly technology and can prepare high-yield TNT samples. Therefore, it may be an important task to examine the potential applications of TNT synthesized by the hydrothermal method for ammonium adsorptive removing from aqueous solution.

The objectives of this study are to examine the potential of TNT to remove ammonium from aqueous solution. The relationship between the alteration in the microstructure of TNT induced by variation of its sodium contents and the change in the ammonium removal capacity of TNT is discussed. The thermodynamic and

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kinetic parameters of the ammonium adsorption process are calculated, in order to examine the mechanisms for removing ammonium from aqueous solution onto TNT.

2. Materials and methods

2.1. Preparation and characterization of TNT samples

TNT (Fig. 1) was prepared using a hydrothermal process similar to that described by Kasuga et al. [9,10] and the detail procedures were reported in our previous investigations [13,15]. After hydrothermal reaction, the precipitate was separated by filtration and washed with the HCl solution and deionized water. It was expected that acid treatment would play an important role in controlling the amount of sodium ions remaining in the TNT. In this study, a series of acid washing concentrations, including 0.1, 0.01, 0.001, 0.0001, and 0.00001 N, was used to prepare TNT with distinct residual sodium contents. The amount of residual sodium ions was listed in Table 1. For convenience, we denoted the TNT treated with acid concentrations of 0.1, 0.01, 0.001, 0.0001, and 0.00001 N as S-1 to S-5, respectively (see Table 1). The acid-washed TNT samples were dried in a vacuum oven at 110 °C for 8 h and stored in glass bottles until used.

Effects of the remnant sodium contents on the microstructures of TNT samples were characterized with transmission electron microscopy (TEM), X-ray diffraction (XRD), and nitrogen adsorption-desorption isotherms (Fig. 2) [13,15]. According to the TEM images of TNT samples, it can be experimentally concluded that when the sodium content is greater than 1.21 wt.% (or the acid washing concentration is smaller than 0.01 N), the nanotubular structure can be well-preserved and the morphological characteristics of TNT samples are rather similar. On the other hand, according to the XRD profiles of S-3 to S-5, a characteristic peak is observed at approximately $2\theta = 10^\circ$, which is considered to correspond to $\text{H}_2\text{Ti}_3\text{O}_7$ or $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ crystals. Moreover, for S-2, the peak at approximately $2\theta = 10$ becomes diffuse and for S-1, this characteristic peak does not exist; instead a peak corresponding to anatase-type crystal is observed. From both the TEM image and XRD pattern of S-1, it can be concluded that when the sodium content of TNT is approximately 0 wt.% (meaning a nearly complete proton exchange), the nanotubular structure of titanates may be destroyed. The BET surface area and pore volume of the TNT samples were listed in Table 1. As can be seen from Table 1, S-2 (S-1) has the largest (smallest) surface area and pore volume

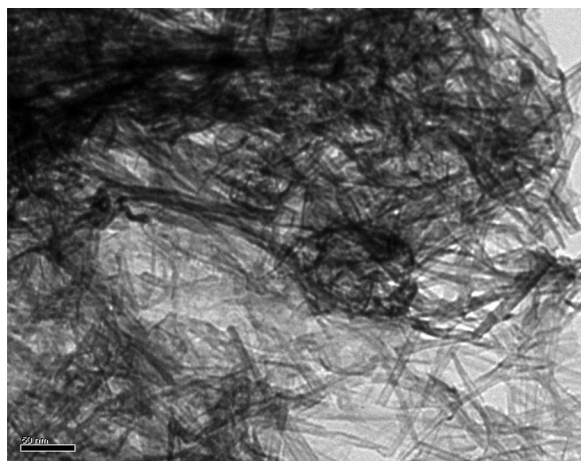


Fig. 1. TEM image of S-5. A large amount of nanotubes with a diameter of 10–30 nm and a length of several hundreds nanometers are obtained.

Table 1

Sodium content, specific surface area, and specific pore volume for the examined TNT samples [13].

Solid	Na content (wt.%)	BET surface area (m^2/g)	Total pore volume (cm^3/g)
S-1	≈ 0	243.3	0.268
S-2	1.21	357.5	1.575
S-3	7.23	241.0	1.091
S-4	7.27	221.8	0.874
S-5	7.35	248.9	1.090

among the examined TNT samples. The sharp decrease in the pore volume of S-1 may be due to the destruction of layered titanate structure, as shown in the disappearance of characteristic peak at approximately $2\theta = 10^\circ$ in the XRD pattern.

2.2. Ammonium removal capacity of TNT samples

Ammonium obtained from the NH_4Cl (analytical grade) was selected as the adsorbate to examine the ammonium removal characteristics of TNT samples. The degree of removal of ammonium from aqueous solution onto TNT samples was obtained by the immersion method. For the immersion experiments, 0.1-g-TNT was added into 100 mL of ammonium aqueous solutions with the desired concentrations (10–300 mg/L). The initial pH value of the solution was adjusted with a NaOH or HCl solution to reach a desirable value. The preliminary experiment revealed that about 1 h was required for the removal process to reach equilibrium, with a reciprocating shaker equipped with a constant temperature controller and a cover to maintain isothermal conditions. The exact concentrations of ammonium in the solutions were determined using ammonium ions selective electrode. The removal capacity of ammonium was then calculated using the relation $Q = V\Delta C/m$, where V was the volume of the liquid phase, m was the mass of TNT, and ΔC was the difference between the initial and final concentration of ammonium in aqueous solution. For the kinetics experiments, the ammonium removal amounts were determined by analyzing the solution at appropriate time intervals. Effects of temperature on the adsorption data were carried out by performing the adsorption experiments at various temperatures (20, 30, and 40 °C).

In this study, the mechanisms for removing ammonium from aqueous solution onto TNT surfaces were examined. The adsorption equilibrium data were fitted into the models of Dubinin-Kaganer-Radushkevick (DKR) [18,19], Langmuir [20], and Freundlich [21].

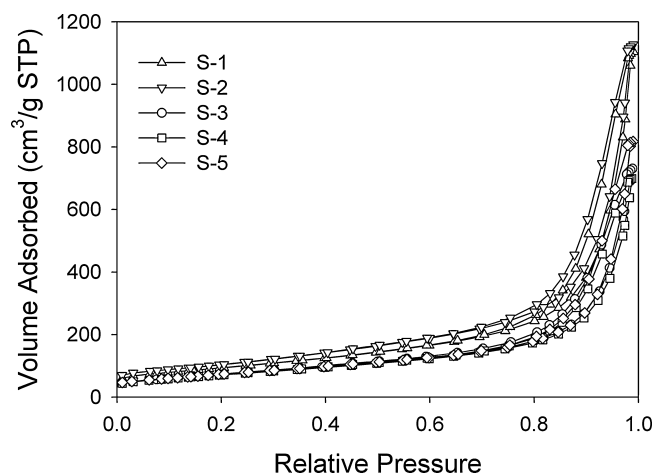


Fig. 2. Adsorption isotherms of nitrogen on the examined TNT samples.

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