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Sorption of organic compounds with different water solubility on octadecyltrichlorosilane-modified titanate nanotubes

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ABSTRACT

The potential of adsorptive removal of organic compounds with a wide range of solubility (S_w) from 55 to 75,000 mg/L onto octadecyltrichlorosilane (OTS) modified titanate nanotube (TNT) was investigated. The examined organic adsorbates included trichloromethane, benzene, toluene, ethylbenzene, propylbenzene, *n*-pentanol, *m*-cresol, and phenol. The adsorbent was prepared via a hydrothermal method to produce TNT that was modified by the OTS. Effects of OTS modified process on the revolution of microstructure and surface chemistry characteristics of TNT were characterized with XRD, nitrogen adsorption–desorption isotherms, and FTIR. It was found that the prepared TNT weakly adsorbed low-S_w organic compounds, but exhibited high uptakes for organic compounds with high S_w values. The OTS-modified TNT (OTNT) possessed both hydrophilic and hydrophobic surface and it could uptake organic compounds with a wide range of S_w values. The isotherms of low-S_w organic compounds on the OTNT approached to linearity and the adsorption capacities were inversely proportional to their S_w values, implying that the dominating sorption mechanism was partitioning. The isotherms of the high-S_w organic compounds were concave downward curves, indicating that the organic compounds were adsorbed on the sites that were not covered by OTS. It was experimentally concluded that the OTNT might be considered to be an excellent adsorbent which could effectively uptake organic compounds with a wide range of solubility due to its amphiphilic characteristics.

1. Introduction

Industrial wastewater may contain various toxic organic substances. The release of toxic organic compounds into the surrounding environment may cause increasing concern about their toxic effects on human health. Many methods have been developed to remove these toxic organic compounds. Because most of the toxic organic compounds are difficultly biodegraded, adsorption becomes a common advance treatment process to remove these organic compounds. Activated carbon has become known as one of the most effective adsorbents for the removal of organic compounds from aqueous solutions due to its high surface area, microporous structure, and high degree of surface reactivity. However, activated carbon often needs high operation cost. A number of investigators intend to develop new adsorbents to remove organic compounds in the wastewater [1–7].

In the wastewater, the organic contaminants may possess either hydrophilic or hydrophobic characteristics. However, most adsorbents exhibit specific adsorption selectivity for hydrophilic or hydrophobic adsorbates due to their unique surface chemical characteristics. When the adsorbents are modified with other organic substances (such as silanes or surfactants), the surface chemical properties of adsorbents as well as their adsorption ability and capacity are altered. As a result, a number of investigators have improved the surface characteristics of adsorbents modified by organic substances to enhance the adsorption efficiency toward the specific organic compounds [8–10]. Among those modification processes, some researchers intended to develop amphiphilic adsorbents that can adsorb both hydrophilic and hydrophobic organic compounds simultaneously to remove a wider range of organic compounds from wastewater [3,11].

Recently, Kasuga *et al.* [12,13] proposed the preparation of TiO_2-derived nanotubes by a hydrothermal treatment of TiO_2 powder in 10 M NaOH aqueous solution. This method does not require any templates and the obtained nanotubes have small diameter of *ca.* 10 nm and high crystallinity. Because TNT derived from hydrothermal method possess ion-exchange property, it could offer a

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special environment for adsorption of cations, such as basic dyes and heavy metal ions, through the cation exchange mechanism [14,15]. Moreover, since the TNT is characterized by a high specific surface area and pore volume, it also offers a special environment for the removal of volatile organic compounds through the adsorption process [16]. However, since TNT hydrothermally synthesized from TiO_2 is rich in OH group, the obtained adsorbates can possess a hydrophilic surface [4]. When the TNT is used to adsorb the hydrophobic organic compounds, the surface of TNT needs to be modified by other organic substances. In such a case, the organic substance covering on the TNT surface produces an organic phase which acts as a partitioning medium which non-ionic organic molecules partition into it from water. Accordingly, organic adsorbates with the different S_w values would have different sorption mechanisms and sorption capacities when they are sorbed by the organic substance modified TNT. In this study, the hydrothermal derived TNT is modified with hydrophobic *n*-octadecyltrichlorosilane (OTS) to change their surface chemical characteristics. Because OTS forms self-assembled monolayer on the TNT surface, the modified-TNT possesses the hydrophobic surface [17,18]. The OTS-modified TNT (OTNT) is used to adsorb the organic compounds with various S_w values (from 55 to 75,000 mg/L). The sorption mechanisms and capacities of the examined organic compounds on the TNT and OTNT are discussed. The obtained results can be applied to develop a new adsorbent that can uptake the organic compounds with the wide range of S_w values.

2. Materials and methods

2.1. Preparation and characterization of TNT and OTNT

TNT was prepared using a hydrothermal process similar to that described by Kasuga *et al.* [12,13]. The TiO_2 source used for the TNT was commercial-grade TiO_2 powder P25 (Degussa AG, Germany), with a crystalline structure of *ca.* 20% rutile and *ca.* 80% anatase and a primary particle size of *ca.* 30 nm. In a typical preparation, 6 g of TiO_2 powder were mixed with 120 mL of 10 M NaOH solution, followed by hydrothermal treatment of the mixture at 150 °C in a 200 mL Teflon-lined autoclave for 24 h. After hydrothermal reaction, the precipitate was separated by filtration and rinsed with 600 mL of distilled water. The obtained TNT sample was immersed with 1000 mL of 0.001 N HCl solution for 10 h. The acid-washing TNT was rinsed with distilled water until chloride was not measured. The synthesized TNT samples were dried in an oven at 110 °C for 8 h and stored in glass bottles until used.

The OTNT was obtained with the addition of 1.0 g of TNT into 50 mL toluene solution containing 500 μmol OTS [$CH_3(CH_2)_{17}SiCl_3$, Merck]. The solution was stirred for 30 min and then separated with 0.2 μm filter. The solid was rinsed with ethanol and chloroform (95%). Finally, the solid was placed in an oven at 110 °C for 5 h to obtain the powder of OTNT.

Transmission electron microscopy (TEM) analyses were conducted to investigate the morphologies and microstructures of the titanate samples with a H-7500 electron microscope (Hitachi, Japan) using 120 kV accelerating voltage. To understand the effects of OTS attachment on the surface chemical properties of TNT, the surface hydrophobicity of the TNT and OTNT was examined. Both TNT and OTNT were added separately into an immiscible mixture of *n*-hexane and water. After shocking each mixture, it was then left under static conditions for 24 h to observe the hydrophilic or hydrophobic surface for the adsorbents. Moreover, the contact angle was detected by an FACE CA-D contact angle meter (Kyowa Interface Science Co.) to demonstrate the observed result. The particle size and morphology of the TNT and OTNT were visualized using a field emission scanning electron microscopy (SEM, JEOL:JSM-6700F). X-ray diffraction (XRD) patterns were obtained on a Thermal ARL X-ray diffractometer (Thermo, France) equipped with a CuKα radiation source and a graphite monochromator. The patterns were used to determine the identity of any crystalline phase or microstructures in the TNT and OTNT samples. In addition, X-ray photoelectron spectroscopy K-Alpha (XPS K-Alpha, Thermo Fisher Scientific) was used to analyze the element composition, Fourier transform infrared (FTIR, Perkin Elemer Model 1600) was used to detect the functional groups on the surface, and nitrogen adsorption–desorption isotherms (Micromeritics TriStar 3000) were used to obtain the changes in surface and pore structure.

2.2. Adsorption experiments

All of the selected organic adsorbates were obtained from Merck in analytical grade or better; they were divided into two groups according to their S_w values. The organic compounds with the relatively lower S_w values include propylbenzene, ethylbenzene, toluene, benzene, and trichloromethane. The organic compounds with the relatively higher S_w values include *n*-pentanol, *m*-cresol, and phenol. The pertinent physicochemical properties of the examined organic compounds are listed in Table 1.

To avoid competitive adsorption, each adsorption experiment was run with single component. The 0.2 g of adsorbent was mixed with distilled water (50 mL) in a Teflon centrifuge tube. The target compound was then added into the tube to provide a concentration of approximately 20–80% S_w in the solution. For the organic compounds having S_w greater than 1000 mg/L, the concentrations were limited to less than 1000 mg/L. The examined organic compounds were added directly as neat liquids using a Hamilton microliter syringe or a medicine spoon. The centrifuge tubes were then equilibrated for 48 h in a reciprocating shaker at 180 rpm. The resulting slurries were then centrifuged for 30 min at 9000 rpm ($9020 \times g$) to separate the solution from the solid. For the lower S_w compounds and *n*-pentanol, the concentrations were analyzed using a gas chromatograph (GC). Aliquots of the solution phase (2 mL) were transferred into glass vials containing carbon disulfide (2 mL). These vials were sealed with Teflon foil-lined screw caps and shaken for 3 h on a reciprocating shaker. The extracts were injected into a Perkin-Elmer Clarus 500 GC equipped with a flame ionization detector to determine the equilibrium concentrations of the selected compounds in the solution. The organic compounds were separated using a J&W DB-5 capillary column (30 m × 0.53 mm ID; film thickness: 3.0 μm). Because the extractions of phenol and *m*-cresol with carbon disulfide proceeded with low recoveries (<80%), their concentrations in solution were analyzed directly using a GENESYS 10 ultraviolet (UV) spectrometer. Since the pH values might affect the adsorption capacities of phenol and *m*-cresol, the pH value in the adsorption process was controlled at 5.0, which could avoid the dissociation of phenol and *m*-cresol in the solution. After

Table 1
Molecular weights and water solubility (at 25 °C) of the selected organic compounds.

	Compounds	Molecular weight	Water solubility (mg/L)
Low S_w	Propylbenzene	120	55
	Ethylbenzene	106	152
	Toluene	92.1	515
	Benzene	78.1	1780
	Trichloromethane	119	7900
High S_w	*n*-Pentanol	88.2	22,000
	m-Cresol	108	25,000
	Phenol	94	75,000