

Short communication

Application of titanate nanotubes for dyes adsorptive removal from aqueous solution

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Abstract

The potential of adsorptive removal of basic dyes with titanate nanotubes (TNTs) and acid dyes with surfactant (hexadecyltrimethylammonium (HDTMA) chloride)-modified TNTs were investigated. TNTs were prepared via a hydrothermal method and subsequently washed with HCl aqueous solutions of different concentrations. The prepared TNTs were then mediated by the HDTMA ions through the cation exchange process. Effects of acid washing and HDTMA-modified process on the revolution of microstructure and surface chemistry characteristics of TNTs were characterized with XRD, nitrogen adsorption–desorption isotherms, and FTIR. The adsorption capacities of two basic dyes (two acid dyes) on TNTs (their HDTMA-modified version) at initial dye concentration of 2000 mg/L were measured. It was experimentally concluded that if the amount of Na⁺ in the TNTs was not very low, the TNTs and their HDTMA-modified version might be a good adsorbent for the removal of basic and acid dyes from aqueous solution through the cation and anion exchange mechanism, respectively. The adsorption capacity for basic and acid dyes could reach 380 and 400 mg/g, respectively.

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1. Introduction

Dye wastewaters are recognized as difficult-to-treat pollutants and discharged by a wide variety of sources, such as textiles, printing, dyeing, dyestuff manufacturing, and food plants. Physical adsorption was found to be an efficient and economic process to remove dyes from the wastes streams and also to control the biochemical oxygen demand [1]. The application of adsorption technology utilizing commercial activated carbon has become known and taken a place as one of the most effective technologies for the effluent removal of dyes [2]. However, activated carbon often suffers from high-cost production and regeneration. Therefore, other low-cost adsorbents with high surface area are alternatives [3,4]. In recent years, mesoporous molecular sieves,

such as FSM-16 [5], MCM-22 [6], and MCM-41 [7], have been accepted as the appropriate adsorbents for the removal of dyes from wastewater due to their unique mesoporous pore structure characterized by high specific surface area and pore volume.

Recently, Kasuga et al. [8,9] reported the preparation of TiO₂-derived nanotubes by a hydrothermal treatment of TiO₂ 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 TNTs derived from hydrothermal method possess ion-exchange property and are also characterized by high surface area and pore volume [10,11], they may also offer a special environment for adsorption of large cations, such as basic dyes, through the cation exchange mechanism. Moreover, when the sodium cations are replaced with other organic cations (such as surfactants) from solution onto TNTs, the surface properties of TNTs (and then their adsorption ability and capacity) is altered. For instance, when larger organic cations are used, such as HDTMA ions, the hydrophobic tails interacting with each other may produce an organic phase which acts as a partition medium into which non-ionic organic molecules partition from water. On the other hand,

Abbreviations: AB9, Acid blue 9; AR1, Acid red 1; BG5, Basic green 5; BV10, Basic violet 10; FTIR, Fourier transform infrared; HDTMA, hexadecyltrimethylammonium; TEM, Transmission electron microscopy; TNTs, Titanate nanotubes; XRD, X-ray diffraction

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Table 1
Properties of the examined dyes

Dye	Abbreviation	Chemical formula	Molecular weight	λ_{\max} (nm)
Basic green 5	BG5	$C_{16}H_{17}ClN_4O_2S \cdot (1/2)ZnCl_2$	433	655
Basic violet 10	BV10	$C_{28}H_{31}ClN_2O_3$	479	555
Acid red 1	AR1	$C_{18}H_{13}N_3Na_2O_8S_2$	509	530
Acid blue 9	AB9	$C_{37}H_{36}N_2O_9S_3$	793	630

the hydrophobic bonding by conglomeration of large C_{16} alkyl groups associated with HDTMA can render a positive charge development on the surface of TNTs, from which the organic anions (such as acid dyes) can be removed from aqueous solution with anion exchange mechanism [4]. Since the hydrothermal method above mentioned is a simple, cost-effective, and environmentally friendly technology and can prepare high-yield TNTs, it may be an important task to examine the potential applications of TNTs that are synthesized from such method in environmental protection.

2. Materials and methods

In this study, TNTs were prepared via a hydrothermal method and subsequently washed with HCl aqueous solutions of different concentrations. They were then mediated by the HDTMA ions through the cation exchange process. The potential for the adsorptive removal of basic dyes with TNTs and removal of acid dyes with HDTMA-modified TNTs were examined by measuring the adsorption capacities of two basic dyes (basic green

5 (BG5, Sigma) and basic violet 10 (BV10, Sigma)) and two acid dyes (acid red 1 (AR1, Aldrich) and acid blue 9 (AB9, Aldrich)) on TNTs and their HDTMA-modified version at initial dye concentration of 2000 mg/L, respectively. The properties and the chemical structures of the examined dyes were shown in Table 1 and Fig. 1, respectively. Effects of acid washing and HDTMA-modified process on the revolution of microstructure and surface chemistry characteristics of TNTs were characterized with XRD, nitrogen adsorption–desorption isotherms, and FTIR.

2.1. Preparation of nanotubes

TNTs (Fig. 2) were prepared using a hydrothermal process similar to that described by Kasuga et al. [8,9]. TiO_2 source used for the TNTs was commercial-grade TiO_2 powder P25 (Degussa AG, Germany). In a typical preparation, 6 g of the TiO_2 powder was 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,

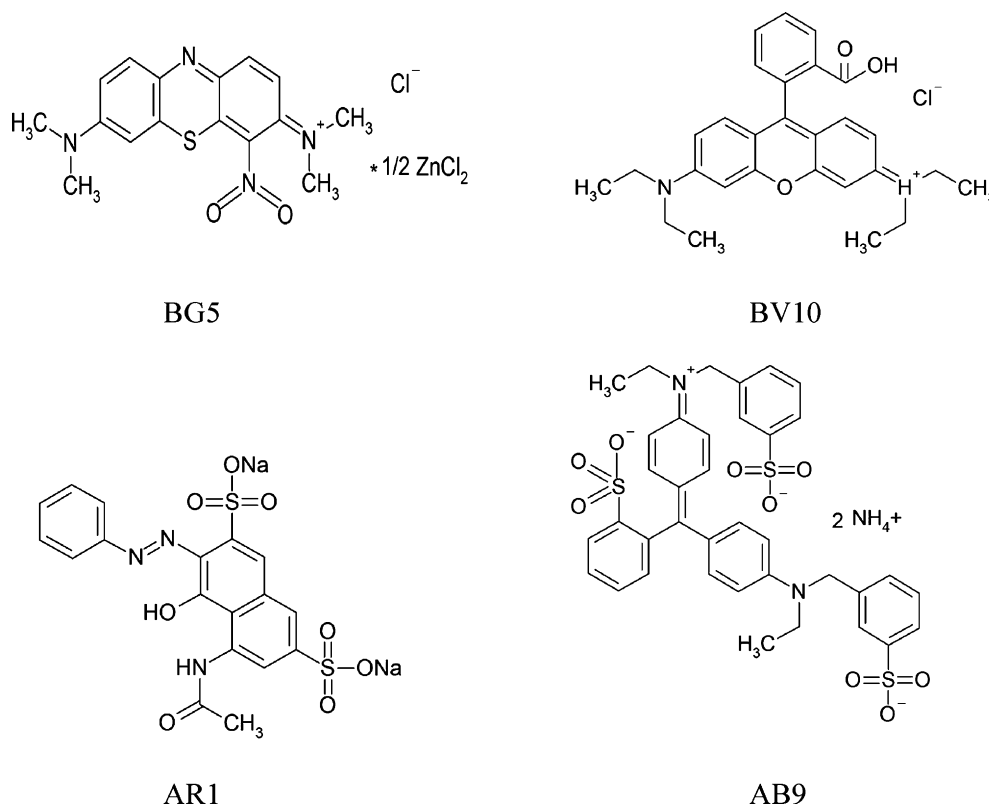


Fig. 1. Chemical structures of the examined dyes.

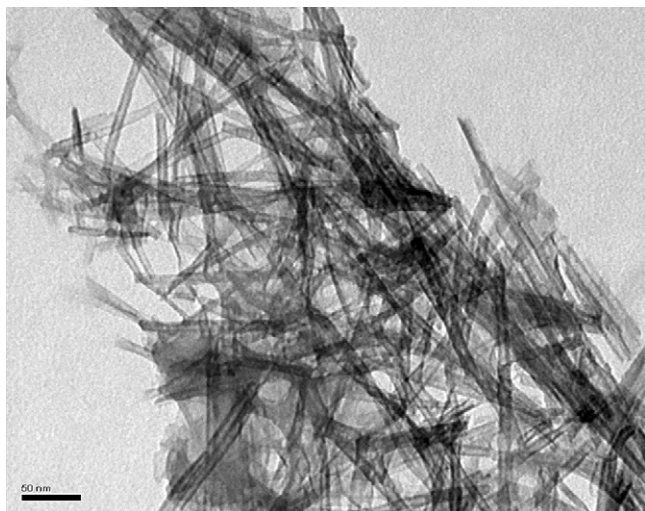


Fig. 2. TEM image of TNTs treated with 0.001N HCl aqueous solution. A large amount of nanotubes with a diameter of 10–30 nm and a length of several hundreds of nanometers are obtained. Moreover, the prepared TNTs possess uniform inner and outer diameters along their length as well as multi-layered and open-ended.

the precipitate was separated by filtration and washed with HCl solution and distilled water. It was expected that acid treatment played an important role in controlling the amount of Na^+ ions remaining in the TNTs. Using aqueous HCl solution of various concentrations, the pH of the sample solution was changed in the range of pH 1–5, and the amount of residual Na^+ ions in the TNTs samples obtained by HCl treatment was measured by atomic absorption spectrometry (Z-5000, Hitachi). The acid washed TNTs samples were dried in a vacuum oven at 110 °C for 8 h and stored in glass bottles until used. The organo-titanate complexes were prepared by replacing the Na^+ on pure TNTs with HDTMA (Aldrich) ions through the cation exchange process. Twenty grams of TNTs was dispersed in 2 L of distilled water and the solid suspension was then treated with HDTMA–Cl solutions in weight ratio of 0.5 HDTMA:1 TNTs. After thorough mixing 6 h, the organo-titanate complexes were washed with distilled water until a negative chloride test was obtained. Then, the exchanged TNTs were freeze-dried and stored at room temperature. We denoted the TNTs treated with acid concentration

0.1, 0.01, 0.001, 0.0001, and 0.00001N as S-1, S-2, S-3, S-4, and S-5 as well as HDTMA-modified counterparts as H-S-1, H-S-2, H-S-3, H-S-4, and H-S-5, respectively (see Table 2).

2.2. Adsorption study

The dyes adsorption data from aqueous solutions at 25 °C were obtained by the immersion method. Dyes were first dried at 105 °C for 24 h to remove moisture before use. For adsorption experiments, 0.1 g titanate sample was added into 100 mL of aqueous dye solution at the concentration of 2000 mg/L. The preliminary experiment revealed that about 4 h was required for the adsorption process to reach equilibrium with a reciprocating shaker. The solution and solid phase were separated by centrifugation at 8000 rpm for 25 min in a Sorvall RC-5C centrifuge. A 15-mL aliquot of the supernatant was taken and analyzed for BG5, BV10, AR1, and AB9 by UV–vis spectrophotometer (UV-160A, Shimadzu) at the wavelengths of 655, 555, 530, and 630 nm, respectively. The adsorption capacity of dyes was then calculated using the relation $Q = V\Delta C/m$, where V was the volume of the liquid phase, m mass of the solid, and ΔC was the difference between the initial and final concentrations of dyes that could be computed simply from the initial and final readings of spectrophotometer.

3. Results and discussion

As can be seen from Table 2, the amount of residual Na^+ in TNTs decreases as the pH value of acid treatment decreases, especially for the S-1 and S-2 samples. Effect of acid treatment on the XRD patterns of TNTs samples are shown in Fig. 3. When the pHs are at 3–5, 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 [12]. Moreover, when the pH is 2, the peak at approximately $2\theta = 10^\circ$ becomes diffuse and when the pH is 1, this characteristic peak does not exist; instead a peak corresponding to anatase-type crystal is observed. The BET surface area, pore size, and pore volume of all examined samples are also listed in Table 2. As can be seen from Table 2, S-2 (S-1) has the largest (smallest) surface area and pore volume among the examined TNTs samples. The sharp decrease in the pore volume

Table 2

Na^+ content, BET surface area, and pore volume of TNTs and their HDTMA-modified version as well as adsorption capacity of BG5 (BV10) and AR1 (AB9) on the examined TNTs

Sample	Na^+ content (wt.%)	Pore structure			Adsorption capacity (mg/g)	
		Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	BG5 (BV10)	AR1 (AB9)
S-1	≈ 0	243.3	10.3	0.268	71.1 (60.4)	19.8 (≈ 0)
S-2	1.21	357.5	14.7	1.575	220.8 (201.9)	9.9 (≈ 0)
S-3	7.23	241.0	14.7	1.091	377.9 (270.5)	19.8 (≈ 0)
S-4	7.27	221.8	13.0	0.874	306.8 (254.8)	≈ 0 (≈ 0)
S-5	7.35	248.9	14.8	1.090	359.2 (294.0)	14.9 (≈ 0)
H-S-1	–	239.4	9.7	0.205	–	≈ 0 (5.9)
H-S-2	–	160.3	11.9	1.000	–	193.1 (37.3)
H-S-3	–	77.9	10.9	0.367	–	381.2 (70.7)
H-S-4	–	45.3	8.9	0.206	–	396.0 (84.5)
H-S-5	–	74.5	12.2	0.397	–	386.1 (84.5)

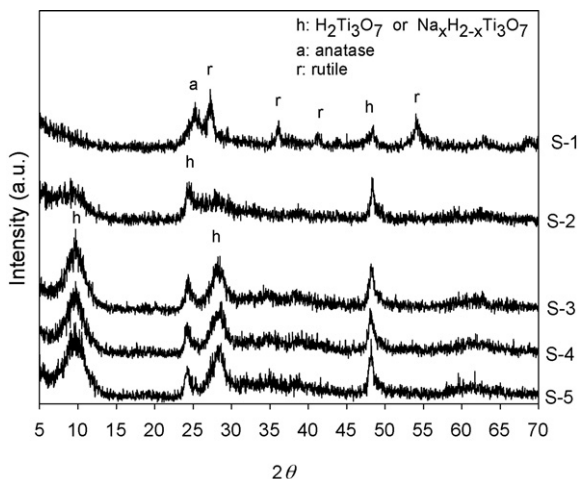


Fig. 3. XRD patterns of TNTs treated with various HCl concentrations.

of S-1 may be due to the destruction of layered titanate structure, as shown in the disappearance of characteristic peak at approximately $2\theta = 10$ in Fig. 3. From Fig. 3 and Table 2, it is found that both the compositions and microstructure of TNTs samples can be changed by controlling the conditions of acid treatment. On the other hand, after HDTMA modification the surface area, pore size, and pore volume of TNTs samples decreases, indicating that the HDTMA may incorporate into the inner parts of TNTs. However, the incorporating amounts of HDTMA are strongly affected by both the cation exchange capacity and the pore volume of TNTs.

Infrared spectra shown in Fig. 4 indicates that there is a large amount of water and hydroxyl groups existed in the TNTs because of the existence of a bending vibration of H–O–H at 1630 cm^{-1} and a strong stretching vibration of O–H at 3400 cm^{-1} [13]. For the HDTMA-modified TNTs, the appearance of the C–H stretching vibrations of HDTMA at 2918 and 2850 cm^{-1} indicates that the bonding between TNTs and HDTMA cations exists [4]. Moreover, because the N–H stretching peak of HDTMA at 3018 cm^{-1} does not appear, the free HDTMA ions does not exist and the addition amount of HDTMA does not exceed the cation exchange capacity of TNTs. It should be noteworthy that because the characteristic peaks of HDTMA are very weak for the H-S-1 sample, the exchanging amount of HDTMA onto H-S-1 may be very low.

Table 2 also shows the adsorption capacity of BG5 and BV10 on the TNTs samples as well as AR1 and AB9 on the HDTMA-modified TNTs samples. For BG5 and BV10, the adsorption capacity of S-3, S-4, and S-5 is larger than that of S-1 and S-2. In general, the adsorption of basic dyes onto TNTs samples is a cation exchange mechanism and the dominating factors controlling the adsorption capacity are the cation exchange capacity and the pore volume of TNTs. Because S-2 possesses the largest pore volume among the examined TNTs samples, the above adsorption results imply that the decrease in the amount of Na^+ may also induce a decrease in the cation exchange capacity of TNTs samples. However, the low basic dyes adsorption capacity of S-1 is closely related to its low pore volume, in addition to the decrease in the cation exchange capacity. On the other hand, it

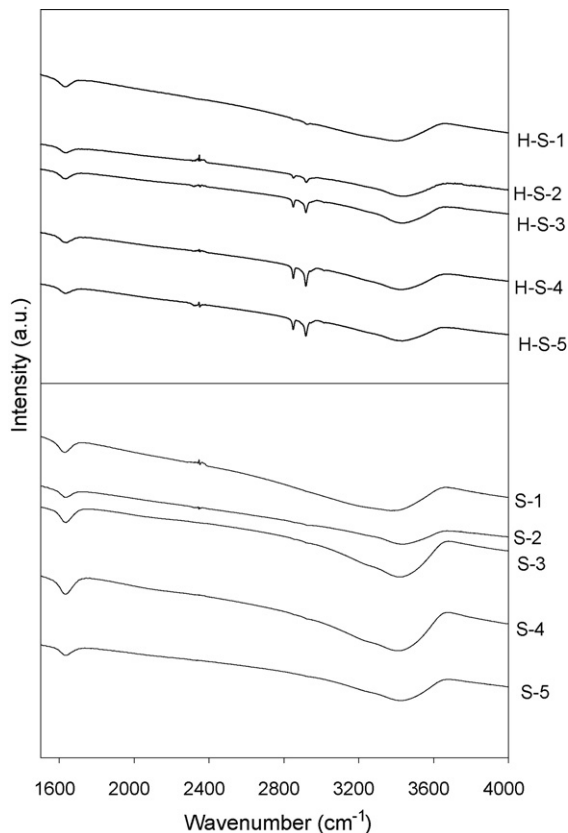


Fig. 4. FTIR spectra of TNTs and their HDTMA-modified version.

can be seen that the adsorption capacity of BG5 is larger than that of BV10 in all examined samples. This result may be ascribed to the smaller size of BG5 and then the more efficient packing array of BG5 in the TNTs. The high adsorption capacity of basic dyes on the TNTs with high amount of Na^+ indicates that TNTs may be a good adsorbent for the removal of basic dyes from aqueous solution with a cation exchange mechanism.

For AR1 and AB9, the very low adsorption capacity of S-1 to S-5 is due to the repulsion forces between the TNTs material negative charge density and the negative charge of the acid dyes. However, when the TNTs are modified with HDTMA, the adsorption capacity of AR1 and AB9 increases significantly (except for H-S-1). In general, when HDTMA cations are used, the hydrophobic bonding by conglomeration of large C_{16} alkyl groups associated with HDTMA can produce a dense packing of HDTMA in the nanotubes and then, a sharp decrease in BET surface area and pore volume. Moreover, the hydrophobic tails interaction of HDTMA ions can also render a positive charge development on TNTs surface, from which the acid dyes can be adsorbed with an anion exchange mechanism. The insignificant adsorption capacity of H-S-1 may be due to the low cation exchange capacity and small pore volume of S-1, causing the exchanging amount of HDTMA may be very low, as shown in Fig. 4. Moreover, it can be seen that the adsorption capacity of AR1 is significantly larger than that of AB9 on H-S-2 to H-S-5 samples. Because the packing of HDTMA in nanotubes may be dense, the adsorbate selectivity induced by adsorbate size may become serious and the adsorption capacity of adsorbate with

large size may decrease significantly, as shown in the case of AB9.

4. Conclusions

It was experimentally demonstrated that if the sodium titanate products did not completely change to hydrogen titanate after washed in acidic solution, the TNTs and their HDTMA-modified version may be a good adsorbent for the removal of basic dyes and acid dyes from aqueous solution through the cation and anion exchange mechanism, respectively. However, it should be noteworthy that for acid dyes adsorbed on HDTMA-modified TNTs, the adsorbate selectivity caused by the adsorbate size becomes obvious due to the dense packing of HDTMA in the nanotubes. The high efficiency for dyes removal by TNTs and their surfactant-modified version with their exceptional adsorption capability suggests that TNTs may have great potential applications in environmental protection.

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