Adsorption and Photocatalytic Degradation of MB over TiO_2 Nanotubes: Influence of Hydrothermal Synthesis Temperature

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Introduction

Dyes and pigments cause heavy pollution to the aquatic environment. Adsorption is an efficient and economic process among several other methods for treatment of dyes-containing wastewater and control of BOD [1,2]. Photocatalytic degradation is a potential alternative for long term and sustainable wastewater treatment as a photocatalyst not only adsorbs but also decomposes the organic pollutants [3]. TiO_2 nanotubes (TNTs) have special ability for the adsorption of large cations, such as basic dye methylene blue (MB) [4]. However, the mechanism of photodegradation of basic dyes over TNTs is still poorly understood. This work focuses on the effect of hydrothermal synthesis temperature on the adsorption and photodegradation performance of MB. Moreover, the reaction mechanism for the photocatalytic degradation of MB on TNTs has also been investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs).

Materials and Methods

The TNTs were synthesized by a general hydrothermal process using commercial-grade TiO_2 powder (P25, Degussa). The TNTs were characterized by TEM, XRD, and N_2 physisorption. MB adsorption experiments were conducted at pH 6. TNTs were added to a20 mg/L MB solution and then the mixture was stirred in dark at 20 ˚C. At appropriate time intervals, aliquots were withdrawn and centrifuged to separate solid particles. The MB concentration in the supernatant solutions was measured by an UV-visible spectrophotometer. The amount of MB adsorbed on TNTS was calculated by the difference between before and after addition of TNTs. The photodegradation of MB was studied after the adsorption-desorption equilibrium was reached by irradiating the mixture solution with a 100 W UV high-pressure mercury lamp and analyzing the change in MB concentration with an UV-vis spectrophotometer. The DRIFT study of photocatalytic degradation was carried out on TNTs with 5 wt.% adsorbed MB with UV light illuminating through the window of the reactor cell.

Results and Discussion

The hydrothermal synthesis was performed in the temperature range of 90-170 ˚C. Hollow, open-ended TiO_2 nanotubes were obtained at a hydrothermal reaction temperature range of 120-150 °C. These TNTs possess inner diameter of 4-5 nm and outer diameter of 8-10 nm with a length of up to several hundred nanometers. At lower temperatures (e.g. 90 °C), the hydrothermal transformation was not complete while at higher synthesis temperature (e.g. 170 °C), the products possess fiber structure with a diameter of 200-500 nm and a length of several micrometers. Kinetic analysis showed that the adsorption performance can be described by a pseudo-second-order equation. The pore properties, rate constant (k), the equilibrium adsorption capacity (Q_e), and photocatalytic performance are shown in **Table 1**.The TNTs synthesized at 120 °C gave the highest apparent rate constant k_{app} of MB photocatalytic degradation, more than 7-times higher than that of TiO_2 fibers synthesized at 170 °C.

Table 1. Properties and adsorption and photocatalytic performances of TNTs.

Synthesis T (°C)	Adsorption kinetics			Photocatalysis		N_2 physisorption	
	Q_e (mg/g)	k ($\times 10^3$, g/mg·min)	R^2	k_{app} ($\times 10^3$, min^{-1})	R^2	Surface area (m^2/g)	Pore volume (cm^3/g)
90	58.5	5.5	0.999	1.7	0.953	290.2	0.74
110	58.7	3.1	0.999	2.6	0.994	334. 6	1.14
120	108.7	2.4	0.999	2.9	0.986	386.1	1.41
130	123.2	0.92	0.998	1.9	0.952	389.6	1.49
140	105.0	1.2	0.999	1.5	0.973	360.2	1.18
150	97.1	2.0	0.999	1.3	0.936	379.4	1.57
160	23.9	26.1	0.999	0.57	0.94	99.6	0.37
170	5.1	-	0.721	0.41	0.915	42.9	0.13

The difference IR spectra obtained by subtracting the absorbance spectrum at initial time from that at different times during UV irradiation gave insight into the mechanism of MB photodegradaion over TNTs. The intensities of MB characteristic bands decreased with reaction time as evidenced with the increase of the intensities of negative peaks, including N-CH_3, C_{Ar}-N, the multiple ring stretching, and C=N at 1229, 1330, 1390 and 1600 cm^{-1}, respectively. At the same time, the characteristic bands reflecting the degradation products were accompanied by the emergence of C=O at 1720 cm^{-1}, carboxylate (COO^-) at 1479 cm^{-1}, and N-H^{3+} at 1526 cm^{-1}. The results also showed that the rate of MB photodegradation over TiO_2-120 was more than 4 times higher than over TiO_2-170 (**Table 1**). Based on the results of DRIFT study, a possible pathway for MB photodegradation on TNTs is proposed, as shown in **Figure 1**.

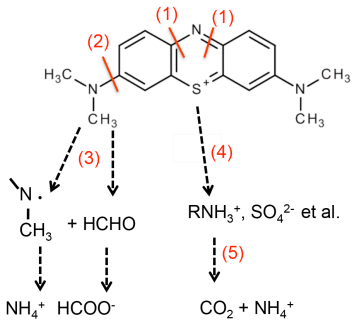

Figure 1. Proposed pathway of MB photocatalytic degradation on TNTs.

Significance

Hydrothermal conditions play a critical role in controlling the physicochemical properties of TNTs. The mechanistic results of MB catalytic degradation could provide useful guidance in the design of metal-doped TNT photocatalysts applied to the visible light range.

References

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