

Using titanium dioxide/carbon nanotubes to remove humic acids in water

Y. P. Tsai*, J. C. Yang, P. C. Chuang, C. C. Chou, J. W. Lin

Dept. of Civil Engineering, National Chi Nan University, 1, University Rd., PuLi, NanTou, Taiwan

*Corresponding author. E-mail: yptsai@ncnu.edu.tw, chi813@gmail.com

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ABSTRACT

This study used multi-walled carbon nanotubes (MWCNTs), TiO₂ and their mixture (TiO₂/CNT) to remove humic acids (HA) in water. The thermodynamic parameters with respect to the adsorption of MWCNTs, including free energy of adsorption (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) changes, are further calculated in the study. The ΔH^0 data showed the adsorption of HA onto MWCNTs is an endothermic physisorption. The ΔG^0 data indicates the adsorption of HA onto MWCNTs was spontaneous and thermodynamically favorable. Photocatalytic experiments showed 60 mgL⁻¹ of HAs were completely degraded and mineralized as CO₂ after 5 h UV irradiation by 0.8 gL⁻¹ of TiO₂, indicating the efficiency of TiO₂ for the removal of HA is better than CNTs. The experiments of TiO₂/CNT indicated the photocatalytic efficiency of TiO₂ in the presence of CNTs was not improved, even worse than TiO₂ alone. However, the photocatalytic efficiency of TiO₂/CNT mixture became better than TiO₂ alone due to the supply of oxygen by aeration, ascribing to the reason that the provided oxygen might be adsorbed on the surface of CNTs and accept e⁻ as well as form •O₂⁻, which also leads to the formation of •OH in the system. Copyright © 2016 VBRI Press.

Keywords: Carbon nanotubes; humic acid; adsorption; titanium dioxide; photocatalyst.

Introduction

Carbon nanotubes (CNTs) have come under intense multidisciplinary study since their discovery [1]. The use of CNTs as an adsorbent to remove organic and inorganic pollutants, such as heavy metals and recalcitrant pollutants, have been widely studied in this decade [2]. Titanium dioxide (TiO₂) is also a feasible nanomaterial for the degradation of organics [3]. UV light illumination of TiO₂ can produce hole-electron pairs on the surface of the photocatalyst. If the hole-electron pairs are separated by energy excitation, the isolated holes may result in oxidation of organics. In the absence of CNTs, the excited hole-electron pairs from TiO₂ have a greater chance of recombining without chemical reaction. Typically, only a small number of electrons (<1 %) and holes are trapped and participate in photocatalytic reactions, resulting in lower reactivity [3-5]. On the other hand in the presence of CNTs, the relative position of the CNT conduction band edge permits the transfer of electrons from the anatase (TiO₂) surface, allowing charge separation, stabilization, and hindered recombination [3, 5]. Thus, it is possible for the photocatalytic reactivity to be enhanced. A few recent studies have shown the advantage of composite TiO₂ and CNTs on the photocatalysis of organics [6-8].

Experimental

Commercial MWCNTs (Nanotech Port Co., Shenzhen China) and TiO₂ (P25, Degussa Co.) were used in the study. Their physical and chemical characteristics can be

referred to Tsai *et al.* [3]. The commercial MWCNTs were purified by heating at 400 °C for 30 min to remove amorphous carbon. HA was analyzed by a high performance liquid chromatography (HPLC, Agilent 1200, USA).

Table 1. Adsorption isotherms data and thermodynamic parameters at different temperature conditions.

Model or Parameter	constants	10°C	25°C	40°C
Langmuir model	Q_{max} (mgg ⁻¹)	94.3	105	119
	b (Lmg ⁻¹)	0.16	0.076	0.127
	R^2	0.979	0.912	0.961
Thermodynamic parameters	ΔG^0 (kJmol ⁻¹)	-5.9	-6.5	-7.1
	ΔH^0 (kJmol ⁻¹)		12.6	
	ΔS^0 (Jmol ⁻¹ K ⁻¹)		65.4	

Results and discussion

Thermodynamic analysis

The adsorption isotherm of MWCNTs used in the study has been analyzed in Tsai *et al.* [9]. To provide in-depth information about inherent change of energies with respect to the adsorption of CNTs, the thermodynamic parameters, including free energy of adsorption (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) changes, are further calculated using Langmuir isotherm data based on the following equations and are shown in **Table 1**.

$$\Delta G^0 = -RT \ln(b) \quad (1)$$

$$\ln(b) = \Delta S^0/R - \Delta H^0/RT \quad (2)$$

where, b is the Langmuir equilibrium constant (L/mg); R is the gas constant ($8.314 \times 10^{-3} \text{ kJmol}^{-1}\text{K}^{-1}$); and T is the absolute temperature in kelvin. ΔH^0 and ΔS^0 were determined from the slope and intercept of the van't Hoff plots of $\ln(b)$ versus $1/T$ [10, 11]. Table 1 shows the thermodynamic parameters at various temperatures for the MWCNTs used in the study. The result suggests the adsorption of HA onto heated MWCNTs is a physisorption because the ΔH^0 (12.6 kJmol^{-1}) was less than 40 kJmol^{-1} , as suggested by Kara *et al.* [12]. Positive ΔH^0 value indicates the adsorption of HA onto MWCNTs is endothermic, which fact is supported by the increase in the adsorption of HA with temperature [9].

Table 2. Thermodynamic data in some past studies with respect to CNTs.

Adsorbate	ΔH_0 (kJmol ⁻¹)	ΔS_0 (Jmol ⁻¹ K ⁻¹)	ΔG_0 (kJmol ⁻¹)	Reference
Trihalomethanes	-1.90	278K: 12.4	278K: -5.36	Lu <i>et al.</i> , 2005 [13]
		288K: 12.6	288K: -5.54	
		298K: 12.6	298K: -5.66	
		308K: 12.4	308K: -5.72	
DCB (As-grow CNT)	5.95	278K: 90	278K: -19.0	Peng <i>et al.</i> , 2003 [14]
		288K: 89	288K: -19.7	
		298K: 90	298K: -20.8	
		278K: 132	278K: -20.4	
DCB (Graphitized CNT)	16.4	288K: 133	288K: -21.8	Peng <i>et al.</i> , 2003 [14]
		298K: 132	298K: -23.0	
		281K: -29.79		
		291K: -31.45		
Procion Red MX-5B	31.6	217	301K: -33.18	Wu, 2007 [10]
			321K: -38.49	
			283K: -5.90	
			298K: -6.85	
Humic acid	12.6	65.4	298K: -6.85	This study
			313K: -7.86	

Furthermore, the positive ΔS^0 in the study implied the degrees of freedom increased at the solid-liquid interface during the adsorption of HA onto MWCNTs. The ΔG^0 values were negative at all of the tested temperatures (10 – 40 °C), indicating the adsorption of HA onto MWCNTs was spontaneous and thermodynamically favorable. Noteworthy, the ΔG^0 values became highly negative when the temperature increased from 10 to 40 °C, revealing the adsorption was more spontaneous at high temperature.

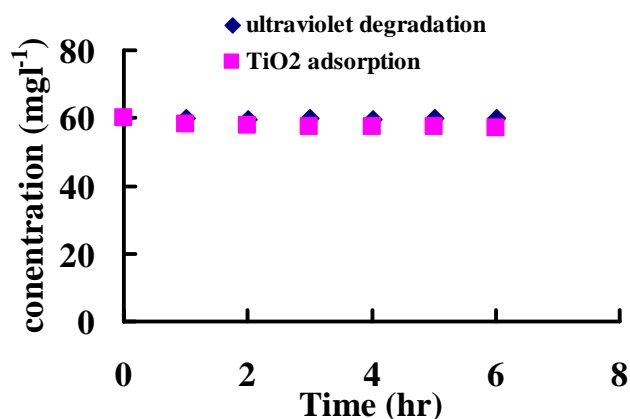


Fig. 1. Background experiments.

Table 2 shows the thermodynamic parameters of past studies. Lu *et al.* [13] used MWCNT to adsorb trihalomethanes and the results showed the ΔH^0 value was negative, whereas others showed opposite results, indicating the ΔH^0 value of the adsorption of organic

compounds onto CNTs might be positive or negative depending on their characteristics of the organics.

Photocatalytic experiments

To understand the adsorption of the TiO_2 without irradiation and the degradation of humic acids under UV irradiation in the absence of TiO_2 , the background experiments were conducted and the results are shown in Fig. 1. Apparently, the degradation of humic acids under UV irradiation in the absence of TiO_2 and the adsorption of TiO_2 without irradiation could be ignored in the subsequent photocatalytic experiments. Further photocatalytic experiments using TiO_2 to degrade HA under the irradiation of UV were conducted and the results are shown in Fig. 2. To understand the mineralization of HA after photocatalysis, TOC was analyzed in the study. Two kinds of TiO_2 dose were tested, including 0.6 and 0.8 gl^{-1} . Fig. 2 shows 60 mg l^{-1} of HAs were completely photodegraded after 5 and 6 h UV irradiation by 0.8 and 0.6 gl^{-1} of TiO_2 , respectively. Based on TOC data also shows 60 mg l^{-1} of HAs were also completely mineralized as CO_2 after 5 h UV irradiation by 0.8 gl^{-1} of TiO_2 .

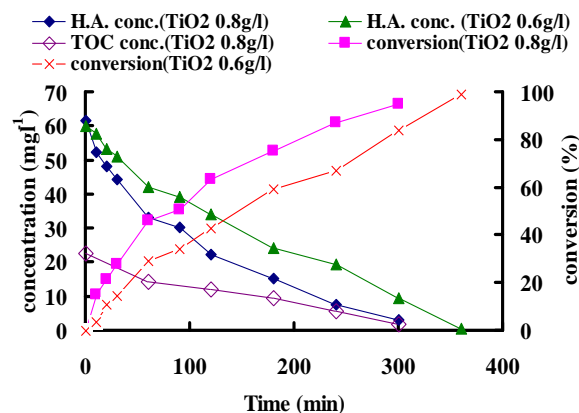


Fig. 2. Photodegradation and mineralization of HA by TiO_2 .

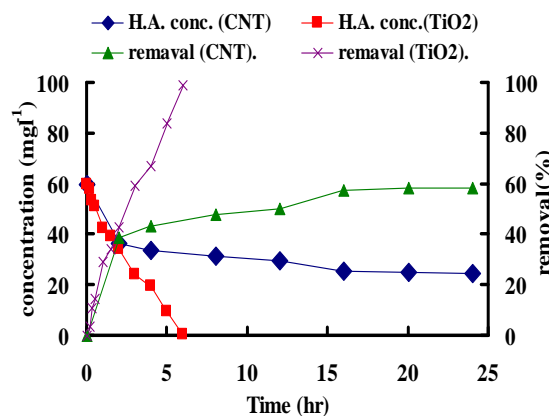


Fig. 3. Comparison of efficiencies of CNT and TiO_2 .

Efficiency comparison of TiO_2 and CNTs

The experimental data about removals of HA by TiO_2 and CNTs are shown in Fig. 3. The removal of HA using TiO_2 as photocatalyst was reaching 100 % after 5 h UV irradiation, whereas only 60 % removal achieved after 24 h

while using CNTs as adsorbent, indicating the efficiency of TiO_2 for the removal of HA is better than CNTs.

Removal of HA by mixture of TiO_2 and CNT

Past studies show the photodegradation of TiO_2 can probably be enhanced by the presence of CNTs. This study tried to mix TiO_2 with CNTs for promoting the degradation rate of HA. The experimental results in Fig. 4 showed 60 mg l^{-1} of HA was completely degraded within 6 h at TiO_2 alone case, whereas only 93 % of HA was degraded at TiO_2/CNT mixture case after 7 h UV irradiation, indicating the photocatalytic efficiency of TiO_2 in the presence of CNTs was not improved, even worse than TiO_2 alone.

The reason of deterioration might be ascribed to the shelter of UV light due to the presence of CNTs. This study further tried to test the photocatalytic efficiency of TiO_2 in the presence of CNTs with extra aeration. The result showed the 60 mg l^{-1} of HA was completely degraded after 5 h UV irradiation, indicating the photocatalytic efficiency of TiO_2/CNT mixture was significantly improved due to extra aeration. The reason of improvement could be ascribed to the supply of oxygen. The provided oxygen may be adsorbed on the surface of CNTs and accept e^- as well as form $\bullet\text{O}_2^-$, which also leads to the formation of $\bullet\text{OH}^-$ in the system [7].

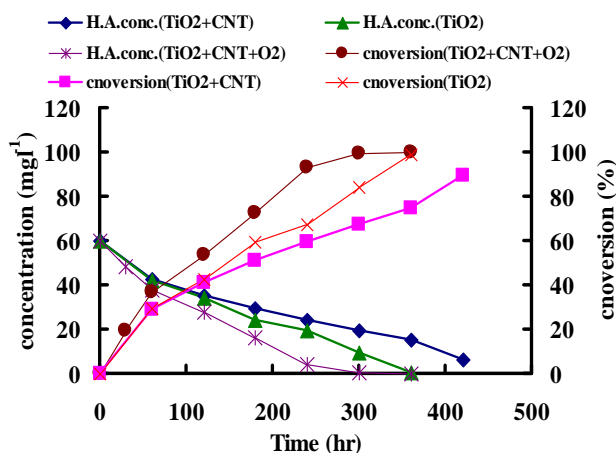


Fig. 4. Efficiency comparison of TiO_2/CNT and TiO_2 alone.

Conclusion

This study used multi-walled CNTs, TiO_2 , and their mixture to remove HAs in water. Results showed the photocatalytic efficiency of TiO_2/CNT mixture became better than TiO_2 alone due to aeration, ascribing to the reason that the provided oxygen might be adsorbed on the surface of CNTs and accept e^- as well as form $\bullet\text{O}_2^-$, which also leads to the formation of $\bullet\text{OH}^-$ in the system.

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