

Applications of TiO₂/Carbonnanotube in Ultrasound System

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1. Introduction

The role of TiO₂ as a catalyst in the sono system can be seen from two viewpoints. TiO₂ act as nuclei for increase of cavitation bubble number. And it can be activated by high temperature and photon energy emitted from cavitation bubble collapseing. Consequently, formation of hydroxyl radicals is increased.^{1,2,3}

However, the degradation rate is limited, because a recombination rate between electro-hole and electron is fast. To overcome this disadvantage, synthesis of TiO₂ with other material has been investigated. The combined material showed high degradation rate because it delays recombination rate.^{4,5}

Carbon Nano Tubes (CNTs) are one of the applicable materials due to large specific surface area and ability to absorb wide range of light compared to TiO₂^{6,7}. Because of these characteristics, CNTs synthesized with TiO₂ enhance the performance as sonocatalyst.

In this study, a new catalyst comprising of TiO₂ and CNTs has been synthesized and applied in ultrasound system. The ratio and dose of TiO₂ and carbon nanotube have been determined by analyzing hydroxyl radical generation rate under different conditions. For the checking efficiency of catalyst, degradation studies of Remazol Black B were also performed. The optimum condition of TiO₂/CNTs was also determined under ultrasound system.

2. Material and Method

TiO₂ (P25, Degussa) and Single Walled Carbon Nano Tubes (SWCNTs, 4.5nm diameter and 0.5-1.5um long) was used for synthesis of catalyst. For the preparation of TiO₂/SWCNTs firstly, SWCNTs were dispersed in the water and sonicated to remove its functional cover. TiO₂ was added and sonicated again. After that SWCNTs and TiO₂ were heated at 80 °C to evaporate the water in the solution and the temperature was changed to 104 °C to dehydrate the composite formed.

Ultrasound was applied to 1L solution in the reactor. Temperature inside the reactor was fixed at 21±1 °C by using Cooling system and pH

was fixed at 5.1. Ultrasonic transducer module (500kHz, 80W, Mirae Ultrasonic Tech.) was placed in the bottom of the reactor.

To measure the hydroxyl radical concentration indirectly, KI dosimetry method was applied. The concentration of I₃⁻ was measured by using UV/Vis spectrometer.

1 ppm of Remazol Black B was dissolved in the solution. The concentration of Remazol Black B was also detected by analyzing its absorbance using UV/Vis Spectrometer.

3. Results and Discussion

Fig. 1 shows that the generation rate of I₃⁻ in different condition. Experiments were performed using TiO₂ alone, different mass ratios of TiO₂/SWCNTs (20:1, 50:1, 100:1, 200:1, 300:1) and without catalyst under ultrasound. Hydroxyl radical generation rates for the given conditions were found to be 5.22, 2.58, 3.2, 8.7, 12.9, 11.7 and 4.27 (× 10⁻² mM/min). From the result, the most effective catalyst is known to be TiO₂/SWCNTs with the ratio of 200:1.

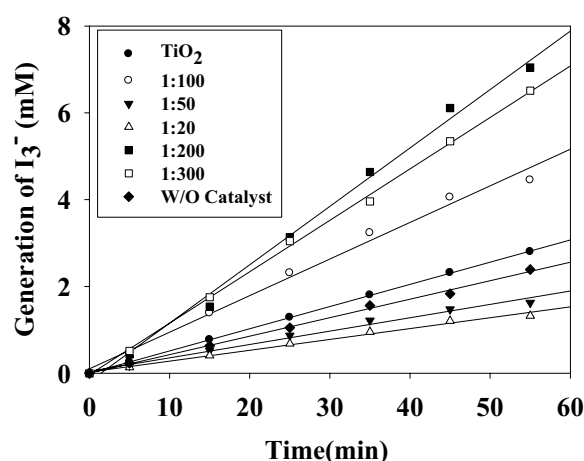


Fig. 1 I₃⁻ generation of each catalysts. Temp=21°C, pH=5.1

Fig. 2 shows the optimal dose of TiO₂/SWCNTs for generation rate of I₃⁻ and degradation rate of dye. The optimal dose of catalyst was observed 0.5 g/L. Several researchers

have reported the optimum dose of TiO_2 to be 1.0 g/L^{8,9,10}. The optimal dose was reduced twice compared to sonocatalysis using only TiO_2 . Because synthesized catalyst has high specific surface area and absorption ability through wide range of light, it shows high performance.

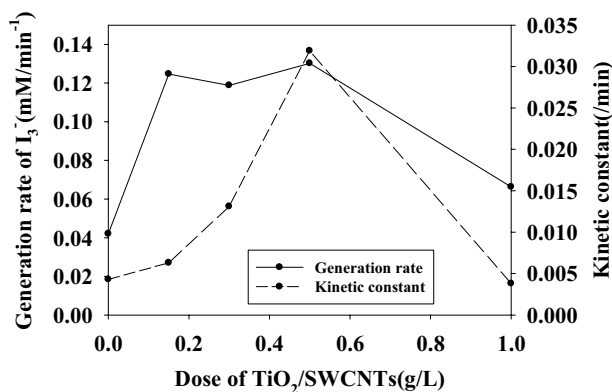


Fig. 2 Values of generation rate of I_3^- and kinetic constants depending on different doses. Temp=21 °C, pH=5.1

Normalized sonocatalytic degradation is shown **Fig 3**. Kinetic constants were calculated according to pseudo-first-order reactions. Kinetic constants of Ultrasound, Ultrasound / TiO_2 , Ultrasound / TiO_2 / SWCNTs processes are 0.43, 1.97, 3.19 ($\times 10^{-2}$ /min), respectively.

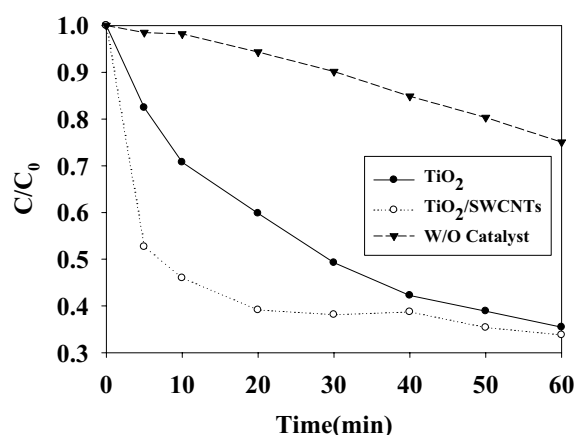


Fig. 3 Normalized ultrasonic degradation profile of Remazol Black B for different systems. Temp=21 °C, pH=5.1

Kinetic constant of ultrasound/ TiO_2 /SWCNTs is 7 times larger than kinetic constant of ultrasound system. A number of cavitation bubbles are generated from the surface of catalyst, and photo energy from cavitation bubble makes hydroxyl radical to photo react with TiO_2 /SWCNTs. The reaction rate of TiO_2 /SWCNTs reaction is 61%

faster than the reaction rate of TiO_2 under ultrasound system. First reason is CNTs specific surface area is bigger than TiO_2 ⁶. Second reason is the combination of TiO_2 and SWCNTs decreases the band gap energy than make more possibility to generate hydroxyl radical in the solution. Band gap energy of TiO_2 is 3.2eV, whereas that of TiO_2 /SWCNTs is 2.29eV with a ratio of 100:1.

Based on the results, it can be concluded that CNTs enhances the catalyst properties of TiO_2 . Moreover, the optimum ratio of TiO_2 /SWCNTs is 200:1 and the optimum dose is 0.5g/L.

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