

## Microbial cellulose as a support for photocatalytic oxidation of toluene using TiO<sub>2</sub> nanoparticles

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**ABSTRACT:** The aim of this study was to investigate the feasibility of toluene degradation using impregnated microbial cellulose (MC) with titanium dioxide (TiO<sub>2</sub>) nanoparticles (MC/TiO<sub>2</sub>). The effects of the initial toluene concentration and ultraviolet (UV) source on the degradation efficiency of toluene have been evaluated. The experimental results showed that the rate of toluene degradation decreased with an increasing of the inlet toluene concentration. After 40 min reaction time, the decomposition rate (%) of toluene decreased from 72.3% to 36.02% for experiments conducted at 100 and 500 ppm, respectively. The degradation efficiency of toluene decreased with application of UVA source instead of UVC source. The toluene degradation efficiency (%) reached to 87.79% and 76.87% for UVC and UVA irradiation, respectively. At initial toluene concentration of 100 mg/L, toluene degradation efficiency for photocatalysis and photolysis processes were 70.2% and 10.65%, respectively; indicating that the photocatalytic degradation efficiency is significantly higher than that of photolytic degradation efficiency. Furthermore, photocatalytic degradation kinetics of toluene was studied and the rates of degradation were found to conform to pseudo-second-order kinetic. As shown in the present study, impregnation of TiO<sub>2</sub> nanoparticles on MC/TiO<sub>2</sub> significantly increases toluene removal for short exposure time. It can be concluded that the MC acted as a local toluene concentrator by adsorbing pollutants from the air stream, and thereby diffusing them to the TiO<sub>2</sub> nanoparticles for photodegradation. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43051.

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### INTRODUCTION

Recently, various studies have been focused on the production and application of microbial cellulose (MC) as a unique kind of cellulose synthesized by bacteria in the genera *Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina*.<sup>1,2</sup> The most efficient cellulose producer is *Acetobacter xylinum*, a gram-negative acetic acid bacteria. Chemical purity is one of the most important properties of MC, which determine the MC from the cellulose of plants.<sup>3</sup> MC has been found various applications in textile, paper, food, medical, and electronic industries, because of the exclusive properties. Cellulose is a polymer of β-1,4-linked glucopyranose units. On the other hand, atmospheric volatile organic compounds (VOCs) raise health concerns because they impart adverse effects on human health and environment.<sup>4</sup> Toluene is a typical VOC, and it is used for the preparation of many compounds such as paints, adhesives, ink, and cleaning compounds; consequently it is found in many industrial waste effluents.<sup>5,6</sup> Inhalation studies have shown that toluene exposure can result in complications to the nervous system, such as reductions in thinking, memory, and muscular abilities, as well as loss of hearing and color vision.<sup>7</sup> Due to its high volatility

and low solubility in water, most of the toluene occurring in natural water and wastewater is eventually released into the atmosphere. Advanced oxidation processes (AOPs) and, more specifically, heterogeneous photocatalysis represent emerging environmental control options for indoor air purification with large application potential.<sup>8,9</sup> Titanium dioxide (TiO<sub>2</sub>)-mediated heterogeneous photocatalysis has become attractive option, with applications including self-cleaning and environmental pollution remediation, mainly due to the hydrophilic properties of TiO<sub>2</sub> and its ability to degrade a wide range of inorganic and organic compounds in both aqueous and gaseous phases.<sup>10–12</sup> The initial reaction step consists of electron–hole pair production by irradiating the semiconductor with light that has energy higher than the band gap; ultraviolet (UV) light is thus needed for TiO<sub>2</sub> activation. Mobile TiO<sub>2</sub> nanoparticles can cause several adverse human health problems. In order to avoid the adverse effects of TiO<sub>2</sub> nanoparticles, efforts have been made to coat TiO<sub>2</sub> thin films onto various substrates such as glass, plastics, clay, and polymers.<sup>13</sup> A more common way to possibly increase the photocatalytic efficiency of TiO<sub>2</sub> consists of adding an inert co-adsorbent. It has been primarily studied either in gas phase

**Table I.** Main Characteristics of MC Biofilm

Characteristics	Amount	Unit
BET	632	Sqm/g
Apparent density	990	g/L
Iodine number	210	-
Moisture	96.28	%

or in aqueous phase in the photodecomposition of organic pollutants.<sup>14,15</sup> A synergistic effect has been already observed by using powdered TiO<sub>2</sub> and activated carbon (AC) in the photocatalytic degradation of toluene.<sup>16</sup> This synergistic effect has been related to the presence of a common contact interface spontaneously created between both solids. This common interface promotes not only an appropriated diffusion of pollutants from adsorbents to photoactive TiO<sub>2</sub>, but also can introduce changes in surface properties of the photocatalyst, and therefore, should play a significant role upon its photoactivity.<sup>17</sup> However, the difficulty in preserving the desired catalytic activity during impregnation limits this application. A cellulose network, shaped as a sheet floating on the medium surface, has been shown to have a high tensile strength, elasticity, resilience, durability, shape retention, and water-binding capacity; furthermore, it is nontoxic and non-allergenic.<sup>18,19</sup> In this work, the unique properties of MC as support for photocatalytic decomposition of toluene in gaseous phase were investigated. Therefore, TiO<sub>2</sub> nanoparticles were impregnated on the MC, and the toluene degradation efficiency under UV-light irradiation was evaluated. Finally, synergistic effects of photolytic and impregnated catalyst (MC/TiO<sub>2</sub>) agents were studied. Also, the kinetics of photocatalytic degradation process was evaluated employing pseudo-first- and second-order rate equations.

## EXPERIMENTAL

### Materials

Glucose, peptone, yeast extract, citric acid, disodium hydrogen phosphate, sodium dodecyl sulfate (SDS), sodium hydroxide, and toluene were obtained commercially from Merck Co. (Germany). The investigated photocatalyst was TiO<sub>2</sub> nanoparticles (P25 Degussa).

### The MC Preparation

In the present study, *Acetobacter xylinum* (ATCC 23768) was used to prepare MC. The culture medium was a Schramm & Hestrin (SH) medium, which consisted of 2% (W/V) glucose,

0.5% (W/V) yeast extract, 0.5% peptone, 0.27% (W/V) Na<sub>2</sub>HPO<sub>4</sub>, and 0.115% (W/V) citric acid. Prior to sterilization at 121°C, the pH of the medium was adjusted to 5.0. The bacterial grown on the agar slants was reactivated at 28°C for 24 h. Cultivation was carried out by selecting a single colony and transferring it to a 500°C flask containing 100 mL of the SH medium and then cultivating at 28°C for 7 days. The characteristics of the MC are listed in Table I.<sup>18,20</sup> The MC biofilms were purified via treatment with 4% sodium dodecyl sulfate (SDS) in deionized water at 70°C for 3 h, and then treatment with 4% NaOH in deionized water at 70°C for 90 min. The samples were rinsed with deionized water at a pH 7 and stored in deionized water at room temperature prior to use.

### Preparation of Impregnated TiO<sub>2</sub> Nanoparticle

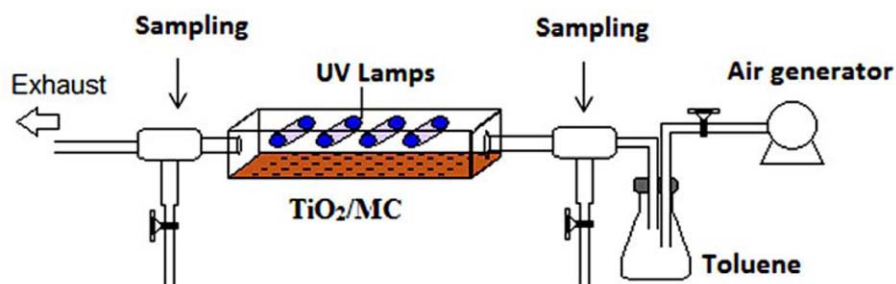
To impregnate the TiO<sub>2</sub> nanoparticle, 5 g of the TiO<sub>2</sub> nanoparticle was mixed in 100 mL distilled water and stirred for 3 min. After that, 5 g of MC prepared via aforementioned section was added. The mixture was poured into a petri dish (3.5 in. diameter) and finally heated in a microwave (Samsung Co.) at 180 W for 15 min.

### Photocatalytic Experiments: Reactor and Set-Up

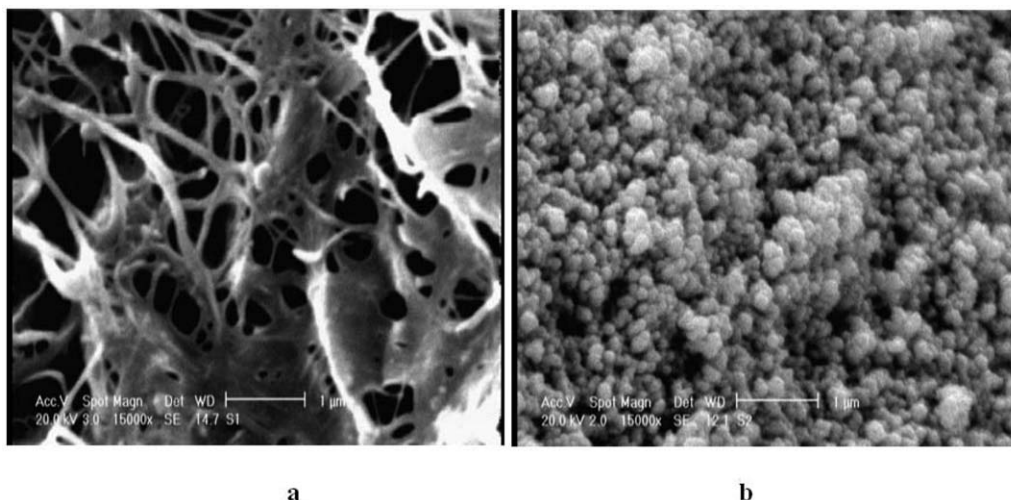
The photocatalytic degradation of toluene was investigated in a rectangular Plexiglass flat-plate photoreactor (length: 34 cm, width: 28 cm, height: 17 cm) operating in its flow-through mode (Figure 1). The area of the film photocatalyst used for each experiment was kept at about 952 cm<sup>2</sup>. Gas sampling points were provided at both the inlet and outlet of the reactor. The UV lamps were placed horizontally at the upper part of the reactor. The temperature in the reactor was kept at 25.0°C ± 0.1°C. A zero air generator (Thermo Environmental Inc. Model 111) was used to supply the air stream, and the inlet gas stream was contaminated with toluene. After the inlet and the outlet concentration achieved equilibrium, the UV lamps were turned on, and the reaction was initiated. Clean humidified air was flushed through the reactor overnight under UV-illumination, after each daily experiment.

### Analytical Methods

The amount of TiO<sub>2</sub> nanoparticle present in the MC was determined from the weight difference (before and after the coating procedure). The surface structure of the MC/TiO<sub>2</sub> was studied using a scanning electron microscope (Philips XL30, Netherlands). EDX analysis was done using a SEM coupled to an X-ray detector for EDX analysis. The specific surface area of the various samples was determined by nitrogen adsorption in a constant volume adsorption apparatus (Micrometrics, ASAP



**Figure 1.** The schematic diagram of the experimental reactor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 2.** SEM micrograph of (a) the virgin MC and (b) after impregnation with  $\text{TiO}_2$  at 15,000 $\times$  magnification.

2021C). The toluene concentrations were determined using a Philips PU-4410 gas chromatograph (GC) equipped with a flame ionization detector. Gas samples of 1 mL that contained the target contaminants were obtained directly from the rubber septum sampling ports using 5-mL Hamilton gas-tight syringes. These gas samples were immediately injected into the GC unit to determine the concentrations. The compounds were separated in a 10% SE30 packed column (1.5 m, 4 mm ID). The temperatures of the injection port and detector were 220°C and 250°C, respectively. Nitrogen gas (30 mL/min) was used as the carrier gas. The sample (100  $\mu\text{L}$ ) was injected into the chromatograph without further treatment.

## RESULTS AND DISCUSSION

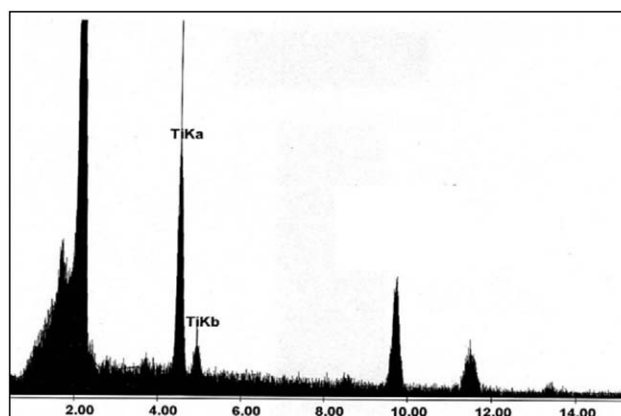
### The Characterization of Composite (MC/ $\text{TiO}_2$ )

Specific surface area measurements of the impregnated MC with  $\text{TiO}_2$  nanoparticle using the Brunauer–Emmett–Teller (BET) method yielded a surface area of 600  $\text{m}^2/\text{g}$ . Figure 2 shows SEM images of virgin MC [Figure 2(a)], as well as the impregnated MC [Figure 2(b)]. In agreement to this study, it was shown that the cellulose has a high crystallinity, a high water absorption capacity and mechanical strength, and an ultrafine network structure, and it is available in an initially wet state.<sup>21</sup> The holes and pores on the surface of MC would help catalyst maintain the characteristics of adsorption and increase the photocatalytic reaction surface area. As shown in the Figure 2(b) the  $\text{TiO}_2$  nanoparticles have been found to form an appropriate film on the MC surface, which shows a high performance support for impregnated  $\text{TiO}_2$  nanoparticles in the decomposition of toluene vapors. The MC acts as a local toluene concentrator by adsorbing pollutants from the air stream, and thereby diffusing them to the  $\text{TiO}_2$  nanoparticles for photodecomposition.<sup>17</sup> It was shown the impregnation of catalysts in a support matrix is an effective strategy to enhance stability of catalyst.<sup>18,19</sup> Moreover, the EDX spectrum of  $\text{TiO}_2/\text{MC}$  shows the presence of two Ti peaks which confirms the availability of the catalyst in the composition (Figure 3). Obtained surface area for MC/ $\text{TiO}_2$  was higher than that of pure  $\text{TiO}_2$  nanoparticles (50  $\text{m}^2/\text{g}$ ) indicating suitability of the impregnation process for increment of

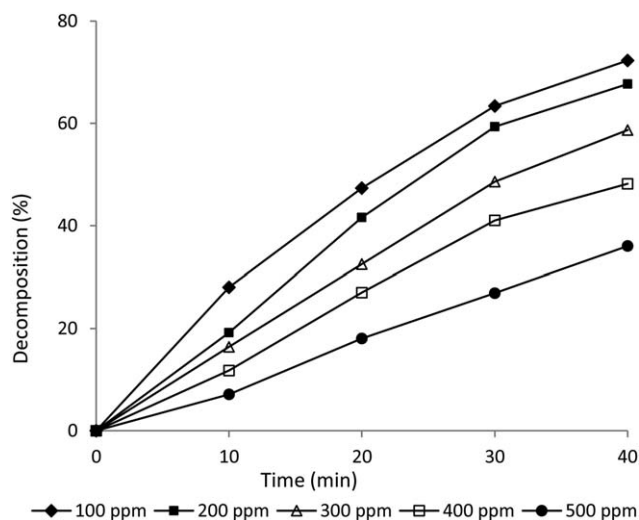
the catalyst surface area. This provides much more reaction sites for degradation of the toluene.

### Effect of Initial Concentration of Toluene

The photocatalytic activity experiments using impregnated MC with  $\text{TiO}_2$  nanoparticle for the photocatalytic degradation of toluene in air were performed at ambient temperature. After the catalyst was placed in the reactor, a small amount of toluene was injected into the reactor. The toluene vapor was allowed to reach adsorption equilibrium with the catalyst in the reactor prior to an experiment. The initial concentration of toluene after the adsorption equilibrium was remained constant until the UV lamp in the reactor was switched on. As MC/ $\text{TiO}_2$  is added into the reactor, the degradation efficiency became significant. Figure 4 shows the degradation efficiency (%) of MC/ $\text{TiO}_2$  for toluene removal at different initial concentrations. The degradation efficiency (%) of the MC/ $\text{TiO}_2$  system after reaction time of 40 min, at initial concentrations of 100, 200, 300, 400 and 500 ppm, was 72.3%, 67.71%, 58.86%, 48.17%, and 36.02%, respectively. Accordingly, it can be concluded that the photocatalytic degradation efficiency of toluene decreased with increasing initial toluene concentration. This behavior can be explained by this fact that in the high concentrations of toluene,



**Figure 3.** EDX result of  $\text{TiO}_2$  nanoparticle coated on MC.

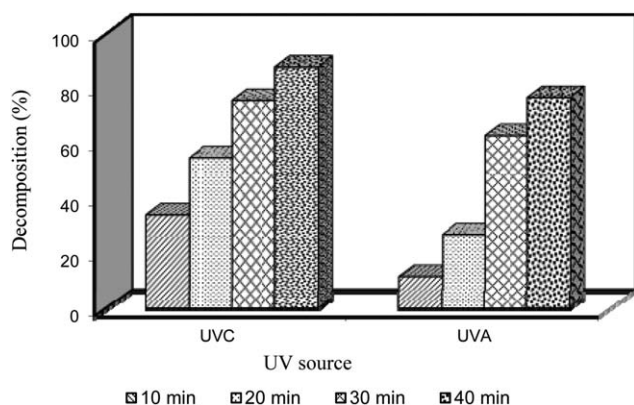


**Figure 4.** Effect of initial toluene concentration on toluene decomposition by photocatalytic process.

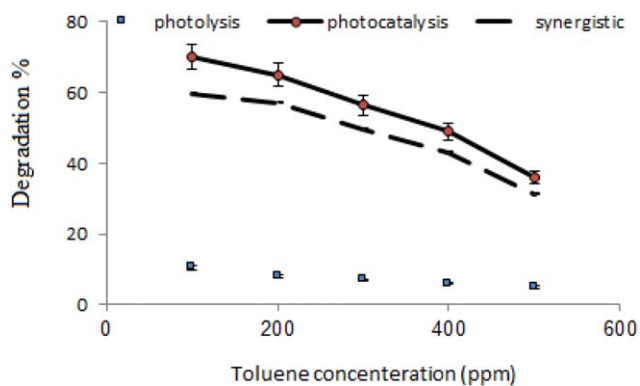
the active reaction sites of the MC/TiO<sub>2</sub> were fully covered with the toluene molecules leading to a reduction of toluene degradation by means of MC/TiO<sub>2</sub>. On the contrary, at lower concentrations of toluene, the toluene molecules were not sufficient to mask the active reaction sites of the MC/TiO<sub>2</sub>.<sup>6</sup> Kim *et al.* (2002) in their study on photocatalytic degradation of VOCs including toluene reported the steep rise of the degradation efficiency at low concentration of the VOCs and the subsequent mild variation at higher concentrations.<sup>22</sup>

#### Effect of UV Source and Impregnated Catalyst (TiO<sub>2</sub>/MC)

UVA and UVC sources were used to evaluate the effect of UV source on degradation efficiency of toluene using MC/TiO<sub>2</sub> nanoparticles at constant initial concentration of 400 ppm. The measured UV intensity of UVC lamps (2.43 mW/cm<sup>2</sup>) was nearly double than that using UVA lamps (1.23 mW/cm<sup>2</sup>). Irradiation intensity is an important factor in photocatalysis. As shown in Figure 5, higher toluene degradation efficiency (%) was observed for UVC light. With an increase of reaction time to 40 min, the toluene degradation efficiency (%) of the photo-



**Figure 5.** Effect of UV source on toluene decomposition rate (%) of MC/TiO<sub>2</sub> process at different reaction times.

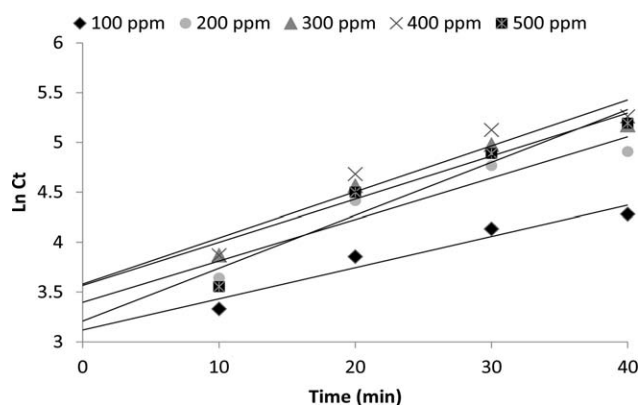


**Figure 6.** Effect of photolytic and photocatalytic on toluene decomposition. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

catalytic process increased from 34.34% to 87.79% and 11.89% to 76.87% for UVC and UVA sources, respectively. Increasing UV intensity produces more photons to excite more electron hole pairs. As a result, more OH• radicals with strong oxidizability were generated to decompose more toluene (Kim *et al.* 2002). In addition, some study showed that TiO<sub>2</sub> particles adsorbed light more strongly for shorter wavelength than longer wavelength and reduced time participating in energy wasting recombination reactions.<sup>23</sup> According to the results of the study, it can be claimed that the absence of TiO<sub>2</sub> nanoparticle lead to significant lower removal efficiency of the toluene.

#### Effect of Catalyst on Toluene Decomposition

The photodecomposition of toluene has been studied under UVC irradiation in the absence and in the presence of the TiO<sub>2</sub> nanoparticles supported on MC. In addition, synergistic effect of photolytic/photocatalytic on toluene decomposition was determined. Results showed the degradation efficiency of the process with catalyst is higher than the process without catalyst (Figure 6). In the case of photocatalysis process, the toluene decomposition rate (%) at initial toluene concentration of 100, 200, 300, 400 and 500 ppm were 70.2%, 64.87%, 57.45%, 49.06%, and 35.71%, respectively. While in the case of the reactor without catalyst (photolysis process) the toluene removal efficiency (%) at initial toluene concentration of 100, 200, 300,



**Figure 7.** Pseudo-first order kinetic models for toluene decomposition by photocatalytic process.



**Table II.** Kinetic Details of Photocatalytic Decomposition of Toluene Using TiO<sub>2</sub> Nanoparticles Supported on MC

Concentration (ppm)	$k_1$ (min <sup>-1</sup> )	$R^2$	Simplified equation
100	0.031	0.93	$C_t = 100 \times e^{-0.0312t}$
200	0.041	0.89	$C_t = 200 \times e^{-0.0415t}$
300	0.043	0.94	$C_t = 300 \times e^{-0.0432t}$
400	0.046	0.90	$C_t = 400 \times e^{-0.0461t}$
500	0.053	0.92	$C_t = 500 \times e^{-0.0531t}$

400 and 500 ppm were 10.65%, 8.54%, 7.65%, 6.98%, and 5.16%, respectively. As seen in Figure 6, the effect of photolytic/photocatalytic synergy on toluene decomposition of toluene is existed. According to results, can be found a synergistic effect of photolytic and impregnated catalyst (MC/TiO<sub>2</sub>) agents is significant. Higher photocatalytic decomposition was obtained in 100 ppm and it was estimated about 59.5%. The synergy was calculated from difference between photolytic and photocatalytic efficiency.

#### Kinetic Evaluation

To determine the kinetic degradation of the toluene, the pseudo-first- and second-order rate equations were evaluated. The results showed that pseudo-first order was fitted to the experimental data. The kinetic equation is defined as following:

$$\ln \frac{C_t}{C_0} = -k_1 t \quad (1)$$

where  $C_0$  is the toluene concentration at the beginning of process;  $C_t$  is concentration of toluene after time  $t$ ; and  $k_1$  is the first-order kinetic constant.

The value of kinetic constant ( $k_1$  min<sup>-1</sup>) with its correlation coefficients ( $R^2$ ) was calculated for each concentration of toluene (Figure 7). The constants values of the pseudo-first-order ( $k_1$ ) are shown in Table II.

#### CONCLUSION

The toluene from air was successfully decomposed by the photocatalytic reaction in a photoreactor using MC/TiO<sub>2</sub> nanoparticles under UV irradiation conditions. The following conclusions can be drawn from our experiments and analyses: (a) The combination of photocatalysis and adsorption is a promising direction for the photodecomposition of toluene; (b) The results showed that degradation efficiency of toluene decreased with increasing initial toluene concentration and decreasing irradiation intensity (using UVA source instead of UVC); (c) The obtained results showed the presence of TiO<sub>2</sub> supported on MC can strongly enhance the photodecomposition of the toluene; (d) We expect the MC/TiO<sub>2</sub> nanoparticle to be utilized with success with other organic pollutants, and further studies are anticipated.

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