Rapid synthesis of Ti-MCM-41 by microwave-assisted hydrothermal method towards photocatalytic degradation of oxytetracycline

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Article history:
Received 17 May 2015
Revised 31 July 2015
Accepted 5 August 2015
Available online 2 February 2016

Keywords:
Oxytetracycline
Ti-MCM-41
Microwave hydrothermal synthesis
Photocatalytic degradation

Abstract

This study employed microwave-assisted hydrothermal method to synthesize Ti-MCM-41, which are mesoporous materials with a high surface area and excellent photocatalytic ability. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and ultraviolet-visible spectroscopy (UV-Vis) were employed. The XRD findings showed that Ti-MCM-41 exhibited a peak at 2θ of 2.2°, which was attributed to the hexagonal MCM-41 structure. The BET (Brunauer–Emmett–Teller) results agreed with the TEM findings that Ti-MCM-41 has a pore size of about 3–5 nm and a high surface area of 883 m²/g. FTIR results illustrated the existence of Si–O–Si and Si–O–Ti bonds in Ti-MCM-41. The appearance of Ti 2p peaks in the XPS results confirmed the FTIR findings that the Ti was successfully doped into the MCM-41 structure. Zeta (ζ)-potential results indicated that the iso-electric point (IEP) of Ti-MCM-41 was at about pH 3.02. In this study, the photocatalytic degradation of oxytetracycline (OTC) at different pH was investigated under Hg lamp irradiation (wavelength 365 nm). The rate constant (Kobs) for OTC degradation was 0.012 min⁻¹ at pH 3. Furthermore, TOC (total organic carbon) and high resolution LC-MS (liquid chromatography–mass spectrometry) analyses were conducted to elucidate the possible intermediate products and degradation pathway for OTC. The TOC removal efficiency of OTC degradation was 87.0%, 74.4% and 50.9% at pH 3, 7 and 10, respectively. LC-MS analysis results showed that the degradation products from OTC resulted from the removal of functional groups from the OTC ring.

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Introduction

Tetracyclines (TCs) are groups of broad spectrum antibiotics that are widely used in humans and livestock to combat diseases. Oxytetracycline (OTC) is a member of this family that is toxic to the ecosystem (Eguchi et al., 2004; Lalumera et al., 2004; Meyer and Boxall, 2006; Watkinson et al., 2009). This kind of antibiotic is ubiquitously used not only in developed...
countries, i.e., Europe or the United States (Ben et al., 2008), but also in developing countries; in China, over 8000 tons of antibiotics are utilized as feed additives each year (Ben et al., 2008). This may cause environmental impacts on surface water, groundwater and soil. In the United States, around 0.15 μg/L, 86–199 μg/kg and 4.0 mg/kg TCs were observed in groundwater and surface water, soil and liquid manure, respectively (Lindsey et al., 2001). In sewage treatment plants, residues of OTC were 0.11, 0.52 and 0.17 μg/L in surface waters, influents and effluents, respectively (Karthikeyan and Meyer, 2006). Li et al. (2008) also reported that OTC has been frequently detected (0.38–2.0 mg/L) in some surface waters that could be used as sources of drinking water. In general, OTC can persist in composting manure for at least five months due to its antibiotic nature, hydrophilic properties and stable naphthalene ring structure (De Liguoro et al., 2003). Even low concentrations of pharmaceuticals released from the environmental matrix into water can pose serious environmental risk. Several surveys have shown that OTC is difficult to remove by conventional water treatment processes, including biological and chlorination processes (Gu and Karthikeyan, 2005; Watkinson et al., 2007). Thus, it is of great importance to develop efficient and cost-effective treatment technologies to degrade such compounds.

Advanced oxidation processes (AOPs), such as ozonation, Fenton, photo-Fenton oxidation, and heterogeneous photo catalysis, have shown great potential as possible complements to conventional water treatment processes. Among these AOPs, heterogeneous photocatalysis, have shown great potential as possible complements to conventional water treatment processes, including biological and chlorination processes (Dutta, 2004; Ko et al., 2011) and CdS (Bao et al., 2007; Jang et al., 2004) exhibited limited application due to its high cost. Therefore, in this study, an energy-saving, frugal and efficient way, namely, a microwave hydrothermal method, was employed to synthesize Ti-MCM-41 (Shi et al., 2011; Wang et al., 2012; Zhang et al., 2012).

In this study, Ti-MCM-41 was synthesized by a microwave-assisted hydrothermal method and evaluated by various characterization techniques, including XRD (X-ray diffraction), FT-IR (Fourier transform infrared spectroscopy), BET (Brunauer–Emmett–Teller), XPS (X-ray photoelectron spectroscopy), UV–Vis (ultraviolet–visible spectroscopy) and TEM (transmission electron microscopy), to investigate its physical and chemical properties. OTC photocatalytic degradation was conducted to examine the photocatalytic ability of Ti-MCM-41. HPLC (high performance liquid chromatography) and TOC measurements were employed to evaluate OTC removal efficiency. In addition, high-resolution LC–mass spectrometry was used to obtain structural information on OTC degradation products and provided information on the degradation mechanism.

### 1. Experimental procedures

#### 1.1. Materials and chemicals

Titanium isopropoxide, sodium silicate (Na$_2$SiO$_3$), hexadecyl trimethyl ammonium bromide (CTAB), and hydrochloride salt of oxytetracycline (TC > 95% purity, molecular weight (MW) 480.90) were purchased from Sigma Company (Sigma Company, St. Louis, MO, USA). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Ke-long Chemical Corporation (Ke-long Chemical Corporation, Chengdu, China). The above chemical reagents were of analytical grade. Acetonitrile of HPLC grade was acquired from Fisher Scientific Corporation (Fisher Scientific Corporation, NJ, USA). All chemicals were used as received without further purification. Solutions were prepared with deionized water.

#### 1.2. Catalyst synthesis

Ti-MCM-41 was synthesized by a microwave hydrothermal method. The cationic surfactant hexadecyltrimethyl-ammonium bromide (CTAB) was used as a template. Titanium (IV) isopropoxide and sodium silicate (Na$_2$SiO$_3$) were used as Ti and Si sources, respectively. The synthesis of titanosilicate was carried out as follows: 4.25 g of CTAB and 5.32 g of Na$_2$SiO$_3$ were dissolved in 30 mL and 15 mL of deionized water, respectively.
water, respectively. These two as-prepared solutions were then mixed followed by vigorous stirring for 30 min at room temperature. After that, 0.45 g titanium (IV) isopropoxide was then dropped into the mixture followed by stirring for 180 min. The pH of the mixed solution was adjusted by 0.1 mol/L HCl to the range of pH 9.5–10.0. Subsequently, the mixed solution was heated by a microwave hydrothermal process at 373 K, 120 W for 180 min. The products were then washed with de-ionized water and dried. To remove the organic species, the obtained samples were sintered at 823 K for 6 hr.

1.3. Catalyst characterization

The crystal structure of Ti-MCM-41 were characterized by X-ray diffraction (Rigaku D/max-2500, Rigaku Corporation, Japan) with Cu Kα radiation (λ = 0.154 nm) operating at a voltage of 40 kV and a current of 100 mA. Diffraction data were recorded at an interval of 0.02° and a scanning speed of 1°/min in the range of 1–10°. The microstructure and morphology of Ti-MCM-41 samples were observed on a TEM (JEOL-JEM-100CX-II, JEOL Ltd., Japan) at an accelerating voltage of 200 kV. The BET (ASAP 2020, Micromeritics, 2020) specific area (S_{BET}) was determined by a multipoint BET method using adsorption data in the relative pressure range from 0.05 to 0.30. The bonding structure of Ti-MCM-41 was analyzed by FTIR (Nicolet 6700, Thermo Fisher Scientific Inc., USA) in the range of 400–4000 cm⁻¹ with a KBr pellet. The absorbance spectrum of Ti-MCM-41 was determined by diffuse reflectance UV–visible spectroscopy (UV-3600, Shimazu, Japan). The measurement was performed at room temperature in the wavelength range of 190–700 nm. XPS analysis was performed in a Perkin–Elmer PHI 1600 ESCA system. Spectra were collected in steps of 0.15 eV. The O 1s and Ti 2p binding energies were referenced to the C 1s peak at 284.6 eV. Zeta (ζ)-potential as a function of the solution pH was used to determine the iso-electric point of Ti-MCM-41. The samples were analyzed using a Nano-ZS90 instrument (Nano-ZS90, Malvern Instruments Corporation, UK).

1.4. Photocatalyst experiment

The photocatalytic performance of as-synthesized Ti-MCM-41 was evaluated by observing OTC degradation under a 100 W (365 nm) low pressure Hg lamp. A 500 mL solution of OTC with concentration of 50 mg/L was added into the vessel. The required amount of the catalyst (1 g/L) was added to the solution. The physico-chemical properties of OTC are shown as follows: at 25°C, the Henry constant is 3.971 × 10⁻²¹ Pa-m³/mol, solubility in water is 1399 mg/L (Xu et al., 2012); octanol–water partition coefficient (Kow) is 0.11–0.34 (Kulshrestha et al., 2004). In order to ensure adsorption/desorption equilibrium in the photocatalytic degradation experiments, the solution was stirred for 90 min in the dark prior to irradiation. After the light was turned on, samples were collected at 30 min intervals and then analyzed by HPLC.

Total organic carbon (TOC) of OTC was determined with a TOC analyzer (TOC–VCPN, Shimadzu, Japan), which utilizes oxidative combustion followed by infrared detection at 650°C. The OTC concentration over time was quantified using HPLC (Agilent 1100 series, Agilent Technologies, Germany) equipped with an Agilent HC-C18 column. The mobile phase (flow rate 0.8 mL/min) was a mixture of oxalic acid, acetonitrile and methanol with the ratio of 3:1:1 (V/V/V). The detection wavelength was 355 nm. To clarify the possible intermediate products of OTC degradation, HPLC/ESI-MS (high performance liquid chromatography/electrospray ionization mass spectrometry) (Bruker-Daltonics, Bremen, Germany) was employed, with a C18 column (Agilent HC-C18, Agilent Technologies, Germany). The mobile phase was a mixture of oxalic acid, acetonitrile and methanol (3:1:1, V/V/V) in an isocratic system that operated at a flow rate of 0.8 mL/min. The mass spectrometer was run in positive ion mode. The dry heater temperature was set at 180°C and the capillary voltage was kept at 3.5 kV.

2. Results and discussion

2.1. Chemical and structural properties

Fig. 1 shows the XRD patterns for Ti-MCM-41 samples synthesized by the microwave hydrothermal method. The samples exhibited a sharp reflection peak corresponding to the (100) reflection at a low angle (2θ = 2.2°), which can be attributed to the long-range order of the hexagonal MCM-41 structure (Shi et al., 2011). Three reflection peaks, signed as (110), (200), and (210) planes, are clearly shown in the 2θ region of 3–7°. Two additional high order peaks were obtained in the case of MCM-41 and Ti-MCM-41 (001) relating to the diffraction planes (110) and (200). In addition, there was a decrease in the intensity of the (200) peak and an evident broadening for all peaks with increasing amounts of Ti, possibly due to a reduction in the long-range order of the structure (Mai et al., 2011). The presence of well-defined XRD peaks indicates the excellent ordering of the mesoporous molecular sieves (Beck et al., 1992). The ionic radius of Ti³⁺ (0.068 nm) is larger than that of Si⁴⁺ (0.041 nm), hence, the substitution of the Ti⁴⁺ ion in place of Si⁴⁺ invariably should distort the geometry around Ti from an ideal tetrahedral coordination (Wang et al., 2012). In addition, the structure will be deformed when a certain amount of Ti atoms are doped into framework (length of Ti–O

![Fig. 1 – Small-angle XRD (X-ray diffraction) patterns of Ti-MCM-41.](image-url)
bond 0.179 nm) and replace Si atoms (length of Si–O bond 0.161 nm) (Shi et al., 2011). Therefore, the change of lattice parameter can be used as evidence that titanium was doped into the MCM-41 structure. Fig. 2a and b shows the TEM images for MCM-41 and Ti-MCM-41, respectively. The pore size of Ti-MCM-41 is around 2.31 nm (as shown in Fig. 2b). Both figures display the presence of a hexagonal, orderly arranged mesoporous structure. The dense honeycomb structure and the long-range shape can also be observed. This uniform pore size ensures a stable structure during the purification and adsorption process. Fig. 3 illustrates the N₂ adsorption–desorption isotherms of the Ti-MCM-41. A hysteresis loop, caused by capillary condensation in mesopores, was observed. This phenomenon proved that Ti-MCM-41 maintains the mesoporous structure after titanium doping (Amama et al., 2005; Mihai et al., 2009; Shi et al., 2011). The sample showed typical type IV adsorption isotherms as defined by International Union of Pure and Applied Chemistry (IUPAC), which is a characteristic of mesoporous materials (Jaroniec et al., 2001; Kruk and Jaroniec, 2001). According to the BET results, the surface area of Ti-MCM-41 is 883 m²/g, which is about 16 times larger than P25 TiO₂. This large surface area is advantageous for environmental applications, such as pollutant adsorption. The isotherm showed a sharp inflection at a relative pressure of 0.35 to 0.45, attributed to capillary condensation inside the primary mesopores. This also illustrates the typical meso-structure with uniform pore size distribution and large pore volumes in Ti-MCM-41 (Uphade et al., 2001). Meanwhile, a pronounced hysteresis loop was observed, with a sharp increase in the adsorption branch at relative pressure about 0.9. This is due to capillary condensation in secondary mesopores, which refers to inter-particle pores or significant large cavities (Kruk et al., 1999, 2000). The BET analysis result agreed with the TEM characterization, that is, the pore size of Ti-MCM-41 is about 3–5 nm, which is a little smaller than that of MCM-41 (Kruk et al., 1997; Morey et al., 1996). Fig. 4 shows a comparison of FTIR spectra for Ti-MCM-41 samples synthesized by microwave-assisted hydrothermal and traditional hydrothermal methods, respectively, in the range of 480–4000 cm⁻¹. The broad bands at 1080 and 810 cm⁻¹ are assigned to asymmetric and symmetric stretching vibrations of Si–O–Si bonds, respectively (Kong et al., 2004; Takahashi et al., 2000). The band at 470 cm⁻¹ is attributed to the tetrahedral bending vibration of Si–O–Si bonds (Schacht et al., 2004). These characteristic peaks were similar to the absorption bands for the typical silicon-oxygen

![Fig. 2](image-url) TEM (transmission electron microscopy) images of (a) MCM-41 and (b) Ti-MCM-41 molecular sieves.

![Fig. 3](image-url) Nitrogen adsorption–desorption isotherms and pore size distribution curves Ti-MCM-41 molecular sieves.

![Fig. 4](image-url) FTIR spectra of MWH-Ti-MCM-41, TH-Ti-MCM-41 and TH-MCM-41. FTIR refers to Fourier transform infrared spectroscopy; MWH refers to microwave-assisted hydrothermal method; TH refers to traditional hydrothermal method.
structure of MCM-41 (Kong et al., 2004). An absorption band at approximately 965 cm\(^{-1}\), which is commonly associated with tetrahedral Ti, could be ascribed to the stretching vibration of SiO\(_4\) tetrahedra bonded to a titanium atom through Si–O–Ti bonds (Kruk et al., 1997; Lafond et al., 2004; Prasad et al., 2006; Shi et al., 2011). This absorption band is associated with Si–OH groups perturbed by metal ions, such as Ti ions. Titanium was integrated into the framework after the microwave-assisted hydrothermal treatment, as evidenced by a band due to Ti–O–Si bonds at approximately 1628 cm\(^{-1}\) (Schacht et al., 2004). A clear band at 3480 cm\(^{-1}\) is observed due to the stretching vibration of isolated Si–OH groups, located mainly at the surface of the inner walls of the MCM-41 channels (Wagner, 1976). UV–Vis spectroscopy is a powerful method for characterization of the coordination environment of titanium in a mesoporous framework (Melero et al., 2005; Ricchiardi et al., 2001). The UV–Vis spectra of Ti-MCM-41 and MCM-41 samples are shown in Fig. 5. Band gap (\(E_g\)) can be calculated according to the Tauc formula (Tauc et al., 1970). The band gap of Ti-MCM-41 is about 3.2 eV (inset plot in Fig. 5). Fig. 5 shows that MCM-41 weakly absorbed both ultraviolet and visible light, while Ti-MCM-41 has a strong absorption in the ultraviolet light region (<400 nm). The absorption band observed in the region of 260–280 nm suggests the presence of small amounts of polymerized Ti–O–Ti species existing with tetrahedral Ti sites (Cai et al., 2011). Clearly, tetrahedral coordination of Ti(IV) is prevalent in Ti-MCM-41 synthesized under microwave irradiation conditions. In general, there is a good correlational relationship between light absorption and photocatalytic activity. Stronger light absorption is associated with higher photocatalytic activity. The UV–Vis DRS spectra results confirmed that Ti atoms were entirely substituted into the silica framework. XPS spectra were recorded for detailed investigation of the chemical state of the elements on the surface of Ti-MCM-41. There is an intense peak at 533 eV, which is attributed to O 1s from Si–O–Si linkages (Barr, 1990). The binding energy of O 1s gives a peak at 529.7 eV for anatase TiO\(_2\), attributed to Ti–O–Ti bonds (Shi et al., 2011). Fig. 6 illustrates the Ti 2p XPS spectrum recorded from the Ti-MCM-41. The spectrum shows two spin-orbit doublet (2p1/2 and 2p3/2) peaks. The binding energy for the Ti (2p3/2) and Ti (2p1/2) peaks was 459 and 465 eV, respectively. The difference in the binding energy between the Ti (2p3/2) peak and Ti (2p1/2) peak was 6 eV, which was similar to that reported in the literature (Riggs and Davis, 1979). The XPS spectra demonstrates that octahedral coordinated titanium species of TiO\(_2\) do not form on the external surface of the series of Ti-MCM-41 materials (Blasco et al., 1995), which is consistent with the results of FTIR spectra. In addition, the atomic percent of Ti ranges up to 0.41% (Table 2), a result that is similar to previous research (Joshi et al., 2008). The photocatalytic properties of Ti-MCM-41 increase with increased Ti content (Wang et al., 2012; Shi et al., 2011). The amount of titanium species in higher coordination rises gradually with the increase of titanium content, with no extra framework titanium formation. The rich Ti(IV) sites in the framework, which provide weak Lewis acid sites on the surface, as well as the mesoporous structure with large pore diameter, are significantly advantageous to enhance the catalytic properties of these Ti-MCM-41 materials (Wang et al., 2012). In addition, the small particle size, large surface area and abundant Ti(IV) active centers inside the framework, which provide more weak acid sites, are advantageous to enhance the catalytic properties (Shi et al., 2011). In this study, zeta (\(\zeta\))-potential was used to investigate the iso-electric point (IEP) of Ti-MCM-41 in the range of pH 2–8. Fig. 7 reveals that the IEP of Ti-MCM-41 was at about pH 3.02. Zeta (\(\zeta\))-potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The value of zeta (\(\zeta\))-potential can be related to the stability of colloidal dispersions. In addition, zeta potential indicates the degree of repulsion between adjacent, similarly charged particles in dispersion, and is widely used for quantification of the magnitude of the electrical charge at the double layer. Hence, the surface charge of Ti-MCM-41 was positive when the pH of solution was lower than the point of zero charge (pH\(_{ZPC}\) = 3.02). These positive charges could react with the photo-generated electrons and leave the photo-generated holes to oxidize water pollutants, e.g., OTC in this study. Therefore, considering the pH-dependent speciation of oxytetracycline and the IEP of Ti-MCM-41, the initial solution pH in the experiments was set at 3.0.

**Fig. 5 – UV-Vis (ultraviolet-visible spectroscopy) spectra of Ti-MCM-41 and MCM-41; inset plot shows the bandgap (\(E_g\)) of Ti-MCM-41.**

**Fig. 6 – XPS (X-ray photoelectron spectroscopy) spectra of Ti-MCM-41; inset plot shows the Ti 2p XPS spectra.**
2.2. Photocatalytic ability of Ti-MCM-41

In this study, OTC was employed as the target compound for the evaluation of the photocatalytic ability of Ti-MCM-41. OTC is a zwitterionic molecule. The fractions of states with varying degrees of protonation can be calculated by the following equations:

$$\alpha^+ = \frac{1}{1 + 10^{\text{pH}-\text{pK}_{a1}} + 10^{\text{pH}-\text{pK}_{a2}} + 10^{\text{pH}-\text{pK}_{a1}-\text{pK}_{a2}}}$$

$$\alpha^0 = \frac{1}{1 + 10^{\text{pK}_{a1}-\text{pH}} + 10^{\text{pH}-\text{pK}_{a2}} + 10^{\text{pH}-\text{pK}_{a1}-\text{pK}_{a2}}}$$

$$\alpha^- = \frac{1}{1 + 10^{\text{pK}_{a2}-\text{pH}} + 10^{\text{pH}-\text{pK}_{a1}} + 10^{\text{pH}-\text{pK}_{a2}}}$$

$$\alpha^+ = \frac{1}{1 + 10^{\text{pK}_{a1}-\text{pK}_{a2}-\text{pH}} + 10^{\text{pK}_{a1}-\text{pK}_{a2}} + 10^{\text{pH}-\text{pK}_{a1}}}$$

where, $\alpha$ is the fraction of a given species. In other words, OTC has different electric charge states in different pH ranges (Kulshrestha et al., 2004). At pH 3, OTC is almost fully protonated as $\text{H}_3\text{OTC}^+$. When pH increases to 7, the majority of OTC changes to a zwitterionic form (H2OTC) by losing a hydrogen atom at the tricarbonyl group. At pH 10, OTC exists as OTC2$^-$ with a fraction of HOTC. Since pH is one of the important factors affecting OTC degradation pathways, this study examined the photocatalytic degradation of TOC at different initial pH (3, 7 and 10, adjusted by NaOH and HCl).

2.2.1. Photolysis of OTC

Fig. 8a illustrates the photolytic degradation of oxytetracycline at various initial pH values as a function of irradiation time. At pH 3, the degradation rate of OTC is slower than that under neutral and alkaline conditions. This may be because the formation of hydroxyl radicals is inhibited in acid conditions (Li et al., 2008). At pH 7 or 10, the degradation rate of OTC was enhanced with increasing pH value. The highest degradation efficiency was 64.4% at pH 10 for a 180 min reaction time. This may be because the dimethyl ammonium group turns into neutral charge at pH 10 (OTC$^-\text{C}$) by losing an H$^+$, while the electrons are easily activated to electronically excited states (Zhao et al., 2013).

2.2.2. Photocatalytic degradation of OTC

The photocatalytic degradation of OTC with Ti-MCM-41 was carried out with different Ti-MCM-41 materials at pH 3, 7 and 10, under 100 W Hg lamp illumination. Compared to photolysis alone, the OTC degradation efficiency was improved by adding Ti-MCM-41. Fig. 8b displays the time-dependent degradation of OTC over Ti-MCM-41 at pH 3, 7 and 10. Notably, a dark condition adsorption experiment was conducted before each OTC photocatalytic degradation experiment. Without the presence of illumination, OTC commenced to degrade right after adding catalyst into the OTC solution and then achieved adsorption equilibrium at 90 min. About 32% OTC was adsorbed by Ti-MCM-41. After light was turned on, about
60% OTC was photocatalytically degraded by Ti-MCM-41 in 180 min. This result demonstrated that the MCM-41 material could have effective photocatalytic ability after titanium doping. In addition, the experimental data approximately fit a pseudo-first-order kinetic model with the linear logarithmic expression:

\[
\ln \left( \frac{C_0}{C_t} \right) = kt
\]

where \( C_0 \), \( C_t \), and \( k \) are the initial OTC concentration, OTC concentration at reaction time \( t \), and rate constant, respectively. The calculated rate constants \( (K_{\text{obs}}') \) for OTC photocatalytic degradation at pH 3, 7 and 10 were 0.012 min\(^{-1}\) \((R^2 = 0.9909)\), 0.0087 min\(^{-1}\) \((R^2 = 0.9781)\) and 0.0077 min\(^{-1}\) \((R^2 = 0.9765)\), respectively. Interestingly, the photocatalytic degradation rate of OTC was higher at pH 3 than that at pH 7 and 10. This result is different from the result of the photolytic process alone. According to the zeta-potential results as shown in Fig. 7, the surface charge of Ti-MCM-41 decreases with increasing pH value. This phenomenon was similar to that observed with TiO\(_2\). The surface charge of TiO\(_2\) was found to be positive when the pH of the solution was lower than 6.5 (Ferreira et al., 2001). Fig. 8c shows a comparison of OTC degradation via photolysis and photocatalysis processes. The OTC removal efficiency for photolysis and photocatalysis was 50% and 92%, respectively, under acidic conditions (pH 3). Fig. 8c also illustrates that OTC removal efficiency reached 89.1% after 180 min UV light irradiation at pH 3 when employing TiO\(_2\) photocatalyst, with a rate constant \( (K_{\text{obs}}') \) of 0.0142 min\(^{-1}\) \((R^2 = 0.9676)\). Notably, adsorption equilibrium was achieved at 90 min and the adsorption capacity was found to be 33.6% for Ti-MCM-41, while it was only 14.7% for TiO\(_2\), as a result of the higher surface area for Ti-MCM-41 compared to TiO\(_2\). This result illustrates that a large surface area is beneficial for pollutant absorption. As shown in Table 3, the rate constant \( (K_{\text{obs}}') \) of OTC photocatalytic degradation was 0.012 min\(^{-1}\), which is about 3 times higher than photolytic degradation. Fig. 8b and c shows that the efficiency was relatively low at pH 10 for OTC degradation by Ti-MCM-41. According to the \( \zeta \)-potential results, Ti-MCM-41 presented negative charge at pH 10, while the negatively charged OTC\(^{2-}\) was also the primary form at this pH. Thus, the electrostatic repulsion between Ti-MCM-41 and OTC\(^{2-}\) made adsorption difficult at pH 10.

2.2.3. TOC analysis

The curves of TOC as a function of reaction time at different pH are shown in Fig. 9. The TOC removal efficiency was 87.0%, 74.4% and 50.9% for pH 3, 7 and 10, respectively. The results also agree with the Zeta (\( \zeta \))-potential findings that an acidic condition is favorable for Ti-MCM-41 photocatalytic degradation. A similar
result was also observed in a previous study (Chen et al., 2011). They applied nano zero-valent iron (NZVI) modified by polyvinylpyrrolidone (PVP-K30) to degrade tetracycline, and indicated that the removal efficiency of TOC was consistent with the removal efficiency of tetracyclines at different pH. This may have resulted from sorption and complex formation with Ti-MCM-41. In other words, the overall OTC disappearance in such batch systems therefore includes not only losses from the degradation reaction but also those due to sorption (Burris et al., 1995; Chen et al., 2011).

2.2.4. LC–MS analysis

The determination of the degradation products of OTC was conducted using high resolution LC–MS. Fig. 10 displays the high resolution LC–MS monitoring of the photocatalytic degradation of OTC by Ti-MCM-41 for different retention times. Molecular OTC was eluted at a retention time of 3.98 min, while the retention time was 4.15, 4.17, 7.41 and 7.30 min for Products 1, 2, 3 and 4, respectively. In addition to the anion with m/z of 461.155 which is attributed to the OTC molecule, four anions with m/z of 477.150, 415.149, 318.299 and 274.273 were observed, suggesting that these main intermediates are generated during reaction. Based on the LC–MS results, the preliminary structures of intermediates are proposed in Table 1. Product 1 (m/z 477.150) stems from OTC by the substitution of $\text{OH}$ in an aromatic ring and undergoes further degradation of Product 2 (m/z 415.149) leads to the generation of Product 3 (m/z 318.299) via the loss of N-methyl, carbonyl and formyl groups, due to the low bond energy of N–C and C–O (Jiao et al., 2008). The degradation of Product 3 (m/z 318.299) then leads to the generation of Product 4 (m/z 274.273) via loss of formyl and hydroxyl groups (Chen et al., 2011). Generally, in the degradation, OTC was mainly transformed into the products with similar structures to TCs.

Combining the OTC degradation, TOC analyses and LC–MS results, we can conclude that the Ti-MCM-41 photocatalyst is a feasible material for OTC remediation.

2.2.5. Suggested reaction mechanism

Ti-MCM-41 can be irradiated by photons with energy equal or greater than its band-gap, leading to the generation of electrons ($e^-$) and holes ($h^+$).

$\text{TiO}_2 + \hbar \nu \rightarrow e^- + h^+$

| Table 1 – Proposed degradation products of oxytetracycline (OTC) by Ti-MCM-41. |
|------------------------|------------------|------------------|------------------|
| m/z       | Molecular weight | Formula           | Possible structure   |
| OTC       | 461.154          | 460.43            | $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_9$       |
| Product 1 | 477.150          | 476               | $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_{10}$    |
| Product 2 | 415.149          | 414               | $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_8$      |
| Product 3 | 318.299          | 317.38            | $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_4$      |
| Product 4 | 274.273          | 272.38            | $\text{C}_{18}\text{H}_{24}\text{O}_2$               |

| Table 2 – Element contents of Ti-MCM-41 based on XPS (X-ray photoelectron spectroscopy) analysis. |
|------------------------|------------------|------------------|
| Name    | Peak BE (eV) | FWHM (eV) | Concentration (Atomic%) |
| O 1s     | 533.07        | 3.11      | 60.53                 |
| Si 2p    | 103.85        | 3.11      | 31.64                 |
| C 1s     | 284.98        | 3.38      | 7.42                  |
| Ti 2p    | 458.75        | 1.39      | 0.41                  |

BE: electron binding energy; FWHM: full width at half maximum.
The photo-generated holes could either recombine with electrons or react with OH\(^-\) or H\(_2\)O to form hydroxyl radical (·OH), which is a strong oxidant. Consequently, hydroxyl radicals can oxidize the OTC molecules adsorbed on the Ti-MCM-41 surface. OTC can react with ·OH in an aromatic ring and undergo further loss of N-methyl, amino, carbonyl, formyl and hydroxyl groups due to the low bond energy of N–C and C–O. Finally, the degraded OTC was mainly transformed into the products with similar structures to TCs.

\[
\text{H}_2\text{O} + h^+ \rightarrow \cdot\text{OH} + \text{H}^+
\]

\[
\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2
\]

\[
\text{OH}^- + h^+ \rightarrow \text{OH}
\]

OTC + ·OH → oxidation products

OTC + e\(^-\) → reduction products

According to the discussion above, the proposed degradation pathways of OTC with Ti-MCM-41 and three main degradation products are shown in Fig. 11.

On the other hand, OTC has different electric charge states, which may have an important influence on its photocatalytic degradation, in different pH ranges. OTC is almost fully protonated as H\(_3\)OTC\(^+\) at pH 3. At pH 7, the majority of OTC changes to a zwitterionic form (H\(_2\)OTC\(^+\)) by losing a hydrogen atom at the tricarbonyl group. At pH 10, OTC exists as OTC\(^2-\) with a fraction of HOTC\(^-\). The iso-electric point (IEP) of Ti-MCM-41 was about pH 3.02, as shown in Fig. 7. The surface

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**Table 3 – Rate constants (K\(^{\prime\prime}\)\(\text{obs}\)) for oxytetracycline (OTC) photolysis and Ti-MCM-41 photocatalytic degradation.**

<table>
<thead>
<tr>
<th>pH</th>
<th>K(^{\prime\prime})(\text{obs}) (min(^{-1}))</th>
<th>K(^{\prime\prime})(\text{obs}) (min(^{-1}))</th>
<th>K(^{\prime\prime})(\text{obs}) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Photolysis Ti-MCM-41 photocatalytic TiO(_2) photocatalytic</td>
<td>Photolysis Ti-MCM-41 photocatalytic TiO(_2) photocatalytic</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0043 (R(^2) = 0.988)</td>
<td>0.012 (R(^2) = 0.9909)</td>
<td>0.0175 (R(^2) = 0.9856)</td>
</tr>
<tr>
<td>7</td>
<td>0.0049 (R(^2) = 0.988)</td>
<td>0.0087 (R(^2) = 0.9781)</td>
<td>0.0166 (R(^2) = 0.9941)</td>
</tr>
<tr>
<td>10</td>
<td>0.0055 (R(^2) = 0.989)</td>
<td>0.0077 (R(^2) = 0.9765)</td>
<td>0.0142 (R(^2) = 0.9754)</td>
</tr>
</tbody>
</table>

Temperature 298 K, initial OTC concentration 50 mg/L, light source 100 W low pressure Hg lamp, wavelength 365 nm, and added dosage 0.1 g/L.

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**Fig. 11 – Proposed degradation pathways of OTC.** P1, P2, P3, and P4 refer to Product 1, Product 2, Product 3 and Product 4. OTC: oxytetracycline.
charge of Ti-MCM-41 was positive when the pH of the solution was lower than the point of zero charge (pH_{ZPC} = 3.02). These positive charges could react with the photo-generated electrons and leave photo-generated holes to oxidize OTC. At pH 10, both Ti-MCM-41 and OTC presented negative charge, thus, the electron repulsion between TiO_2 and OTC makes the adsorption difficult, resulting in low degradation efficiency.

3. Conclusions

This study successfully synthesized titanium-doped MCM-41 through a microwave hydrothermal method in 3 hr. This procedure is a time-saving, energy frugal, and environmentally friendly method compared to the traditional hydrothermal method. Ti-MCM-41 retains a hexagonal structure after titanium doping. The appearance of Ti 2p peaks in XPS analysis confirmed the FTIR findings that Ti was successfully doped into the MCM-41 structure. UV–Vis DRS investigation showed the absorption band of Ti-MCM-41 significantly shifted to 330 nm, which is favorable for photocatalytic applications. The Zeta (-)-potential experiment revealed that the ZPC of Ti-MCM-41 is about pH 3.02. The OTC degradation results indicated that Ti-MCM-41 can remove OTC effectively under acidic conditions. The TOC removal efficiency was 87.0%, 74.4% and 50.9% at pH 3, 7 and 10, respectively. The rate constant (K'_obs) for OTC degradation by Ti-MCM-41 (at pH 3) was 0.012 min^{-1}, up to 3 times higher than that for the photolysis process alone. LC-MS results indicated that the functional groups on the OTC ring can be removed by Ti-MCM-41 photocatalytic degradation at pH 3. Risk assessments, such as determination of the potential toxic effects of the OTC degradation products, should be pursued in future research.

Acknowledgments

The authors are grateful for Prof. Luo in South China University of Technology in China for his kind assistance in LC-MS analysis. We acknowledge the financial support provided by the Tunghai University Global Research and Education on Environment and Society (No. 103GREEnS005-2).

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