

Kinetic study on photocatalytic degradation of 2-chlorophenol using mesoporous titania nanoparticles

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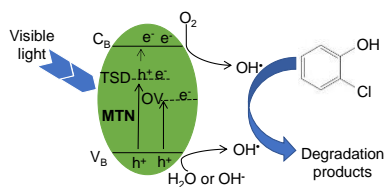
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GRAPHICAL ABSTRACT



ABSTRACT

Photocatalytic degradation is one of advance oxidation process (AOP) techniques where able to break down wide range of the organic pollutants in wastewater. In this study, microwave (MW) – assisted method was used to prepare 450W mesoporous titania nanoparticles (MTN) catalyst. The catalyst was characterized by XRD, UV-DRS and XPS. The photocatalytic degradation of 2-chlorophenol (2-CP) in aqueous solution was studied under visible light irradiation using MTN and the photocatalytic performance of MTN was compared with TiO₂ commercial. The MTN catalyst shows the highest degradation of 2-CP with 100% compared with TiO₂ (50%). This study illustrated that the catalyst works best with dosage 0.0375 g/L in a 10 mg/L solution of pH 5. Kinetic study of MTN was investigated over a concentration range 10 to 100 mg/L using Langmuir-Hinshelwood model. The straight line demonstrated that the degradation follows pseudo-first-order kinetics and this reaction was favourable at low concentration.

Keywords: Mesoporous titania nanoparticles; photocatalytic degradation; 2-chlorophenol; kinetic study

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1. INTRODUCTION

Lately, the issue of environmental pollution has become an issue of concern to society when most of studies have proven environmental pollution undoubtedly affect human health and living things. Most of the pollutants are generated by the industrial factories, where contaminated with toxic and hazardous organic compounds such as biphenyls, organic dyes, pesticides, phenols, pharmaceuticals and herbicides [1]. 2-Chlorophenol (2-CP) is one of the halogenated phenolic compounds has been widely used in industry. Yet, it is classified as an extremely dangerous compound due to its high toxicity, low biodegradability, tendency to bioaccumulate in various water bodies and persistence in the environment [2].

To date, several methods have been used in degrading 2-CP from aqueous pollutants such as biodegradation, adsorption, coagulation and flocculation [3]. Unfortunately, the removal of 2-CP from aqueous pollutants is a complex issue because these treatments not only slow but also could lead to secondary pollutant which are more toxic and required further treatment. Therefore, advance

oxidation process (AOP) such as photocatalytic degradation used semiconductor as photocatalyst commonly used to treat organic and inorganic pollutant in aqueous pollutants [4]. This process consists of absorption of light by a catalyst to initiate the production of hydroxyl radical ($\bullet\text{OH}$) as oxidant to treat the organic compounds which adsorb on the catalyst surface and converted into less toxic compounds.

There are various semiconductors commonly used as photocatalysts such as TiO₂, ZnO, SnO, ZrO₂ and Fe₂O₃ [5]. Among them, TiO₂ show the good potential as photocatalyst prior to its good chemical stability and non-toxic [6]. However, TiO₂ need the utilization of light with energy equal to/or higher than its band gap (3.2 eV) to be more productive during the photocatalytic degradation process and usually its failed to degrade most of the organic pollutants completely in visible light. Thus, self-modification of mesoporous titania nanoparticles (MTN) containing oxygen vacancies (OV) and Ti³⁺ site defects (TSD) is one of the initiatives to improve the TiO₂ properties in light absorption.

The preparation techniques of the MTN catalyst play an important role on the photocatalytic activity. There are some techniques that have been proposed

by the researchers such as precipitation, impregnation, hydrothermal and sol-gel [7]. The sol-gel method recently developed as the most effective ways for preparing the inorganic catalyst because they have more advantages compared to other conventional methods. Combinations of sol-gel process with microwave (MW) – assisted method under various power densities has been proven achieved a good performance on the photocatalytic degradation of 2-CP [8].

Kinetic studies of photocatalytic degradation usually describe by pseudo-first-order and Langmuir-Hinshelwood (LH) in order to determine the influence of initial concentration of the solution. Langmuir-Hinshelwood kinetic describe in term rate of substrate covered the surface of catalyst as well as explained the limitation of mass transfer. In this study, the catalyst properties were determined by XRD and UV-DRS. The kinetic study was studied to determine the competition between adsorption and oxidation during photocatalytic reduction on the catalyst surface.

2. EXPERIMENTS

2.1 Reagents, material and apparatus

Titanium (IV) isopropoxide (TTIP), Degussa P25 and sodium dodecyl sulfate (SDS) surfactant were bought from Sigma-Aldrich. 2-propanol and hydrochloric acid (HCl) were purchased from MERCK, Malaysia. Acetone and methanol were purchased from RPE Reagent pure Erba. Sodium hydroxide (NaOH) and ammonium hydroxide (NH₄OH) were purchased from QREC™ and 2-CP from Alfa Aesar, Germany with 99% purity.

2.2 Preparation of catalyst

The mesoporous TiO₂ (MTN) was synthesized by the microwave-assisted process. 4.68 g of SDS surfactant was dissolved in 720 mL distilled water, 120 mL 2-propanol and 29 mL of 28% ammonia solution. The mixture was stirred continuously for 30 min at 50°C in water bath. After 30 min, the temperature of water bath was increased to 80°C followed by addition of 5.7 mL TTIP and this process was continued for 2 h in water bath in order to dissolve the mixture. After 2 h, the white solution formed was transfer into 1 L beaker and placed in the microwave. The microwave heating was conducted in a domestic microwave oven (Samsung ME711K), which can be operated with power ranging from 100-800 W and frequency of 2.45GHz. The heating process was intermittently continued for 2 h 30 min in order to form a sol-gel catalyst. The microwave power was set with 450 W which then denoted as MTN. The obtained product was collected and dried overnight in oven before calcined at 600°C for 3 h.

2.3 Characterization

The crystalline structures of the catalysts were carried out using a Bruker Advance D8 X-ray powder diffractometer (XRD) with Cu K α radiation $\lambda = 1.5418 \text{ \AA}$ at 2θ angle ranging from 22° to 45°. The phases were identified with the aid of the Joint Committee on Power Diffraction Standard (JCPDS) files. The band gap of the catalysts was measured using UV-Vis diffuse reflectance spectra (UV-Vis DRS) which recorded over a range of wavelength from 250-700 nm using Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer with an integrating sphere. Chemical oxidation of the catalysts was determined using X-ray photoelectron spectroscopy (XPS) conducted on a Kratos Ultra spectrometer equipped with an Mg K α radiation source (10 mA, 15 kV).

2.4 Photodegradation of 2-Chlorophenol

The photoactivity of the catalysts were tested for the degradation of 2-CP. The photocatalytic experiments were performed in a batch reactor with connected to 48 W fluorescence lamp as a visible light source. For photoactivity process, 0.075 g of catalyst was added to the 2-CP solution with desired concentration (200 mL) and stirred for 1 h in the dark condition to achieve adsorption-desorption equilibrium. The initial pH of the solution was pH 5 and the reaction was carried out at 30°C. Then, the reaction was continued for another 5 h under light irradiation under continuous stirring. The concentration of 2-CP in the solution prior to irradiation was used as the initial value for the 2-CP degradation measurements. During the reaction, aliquots of 2 mL were taken out at intervals of 30 min and centrifuged in a Hettich Zentrifugen Micro 120 at 15000 rpm for 15 minutes before being analysed by UV-Vis spectrophotometry (Shimadzu UV-Vis Spectrometer, UV-2600) for the residual concentration of 2-CP. Each set of experiments was performed triplicates. The adsorption band of 2-CP was taken at 274 nm and the the percentage degradation was calculated using the following equation:

$$\text{Degradation (\%)} = \frac{c_i - c_t}{c_i} \times 100 \quad (1)$$

where C_i and C_t are the initial concentration 2-CP and the concentration at time t , respectively.

3. RESULTS AND DISCUSSION

The XRD pattern of TiO₂ and MTN are shown in Fig. 1. A series of XRD peaks for MTN were observed at 25°, 37°, 37.5° and 39° which corresponded to (101), (200), (004) and (112) planes, respectively indicated the presence of TiO₂ anatase phase. Besides, a series of XRD peaks for TiO₂ rutile and brookite phase was detected at 28° (110) and 32.17° (121), respectively. While, only TiO₂ anatase phase were observed at 25.1° (101), 37.1° (200), 37.5° (004) and 38.2° (112) for TiO₂ commercial. The intensity of MTN was higher compared with TiO₂ demonstrated MTN exhibit the

higher crystallinity probably due to good heat distribution in microwave during the synthesis [9].

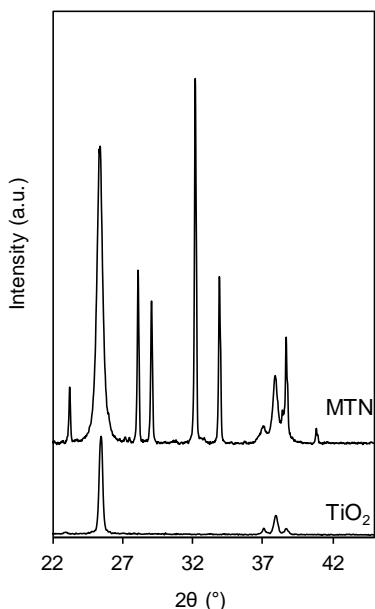


Fig. 1 XRD pattern of TiO₂ and MTN.

The particle size of MTN and TiO₂ are 4.5 and 29.9 nm, respectively, which were calculated using Debye-Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

where D is the particle size, λ is the wavelength of the X-ray radiation (Cu K α =0.1542 nm), k is the shape factor (k=0.94), β is the line width at half-maximum height, and θ is the angular position of the peak maximum, $2\theta = 25.1^\circ$.

Fig. 2 shows UV-Vis DRS spectra of the TiO₂ and MTN. The band gap energy for these catalysts have been calculated from the graph by extrapolating the linear portion of the diffuse reflectance absorption spectrum on the x-axis and follow the equation:

$$E_{bg} = \frac{1240}{\lambda} \quad (3)$$

where E_{bg} is the band gap energy (eV) and λ is the wavelength (nm) obtained from the extrapolating UV-Vis DRS graph. The band gap energy of the TiO₂ and MTN are 3.31 and 3.18 eV, respectively. The band gap energy of the MTN catalyst was lower compared with TiO₂, which could contribute in enhancing their photocatalytic activities in visible light. This is due to narrowing band gap is directly proportional to the photocatalytic activity, thus nano-

particles catalyst is expected to show more activity in the visible region [8,10]. In addition, according to our previous study, the existed of oxygen vacancies (OV) and Ti³⁺ site defects (TSD) in the MTN play an important role for application under visible light irradiation [3].

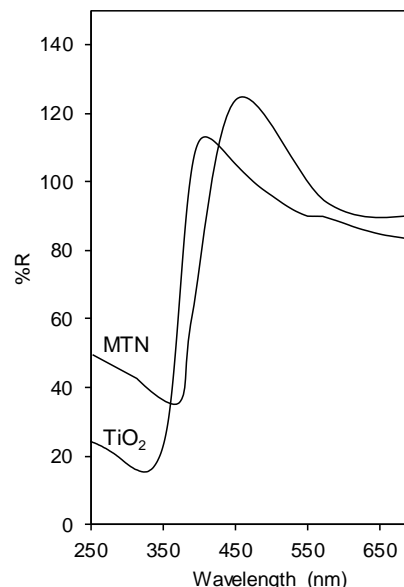


Fig. 2 UV-Vis DRS of TiO₂ and MTN.

Fig. 3 illustrated the XPS spectra of MTN catalyst for Ti2p and O1s. The Ti2p (Fig. 3A) spectrum showed the presence of Ti³⁺ at 458, 459 and 463 eV, while Ti⁴⁺ at 455.7, 458.6 and 465.2 eV [3]. Fig.3A demonstrated the highest ration of Ti³⁺ for the oxidation state instead of Ti⁴⁺. Fig.3B showed the O1s spectrum which showed peaks at 530.6 and 532 eV which attributed to Ti³⁺-O and hydroxide or hydroxyl group (OH⁻), respectively. The number of OV is developed by the existence of OH⁻ in the catalyst [8]. While another two peaks at 530 and 534 eV indicated the presence of Ti⁴⁺-O. These results confirmed the existence of TSD and OV in the MTN.

The photocatalytic activity of TiO₂ and MTN was tested on the degradation of 2-CP under visible light irradiation as showed in Fig.4. It was clearly observed that both catalysts showed better performance in the presence of light where both catalysts illustrated low in the adsorption capability with less than 15% adsorption, indicated light plays an important role to the reaction. MTN illustrated the highest degradation of 2-CP (100%) compared with TiO₂ (50%) probably due to the MTN exhibit higher crystallinity with lower band gap energy. In addition, the presence of TSD and OV also contributed to the photoactivity performance of MTN under visible light irradiation.

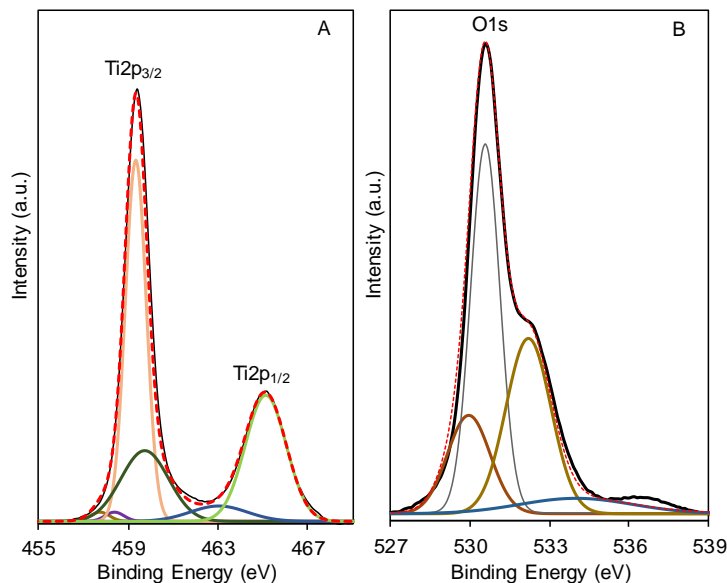


Fig. 3 XPS spectra of (A) Ti2p and (B) O1s of MTN.

The degradation efficiency of the catalyst was also depending on the initial concentration of the substrate. Table 1 shows the effect of initial concentration in the range of 10-100 mg L⁻¹ toward degradation of 2-CP using MTN. The results reveal that the degradation of 2-CP was decreased with increasing initial concentration. These results probably due to increase in initial concentration could inhibited light penetrating to the surface of the catalyst and thus reduced the formation of the hydroxyl radicals that play such an

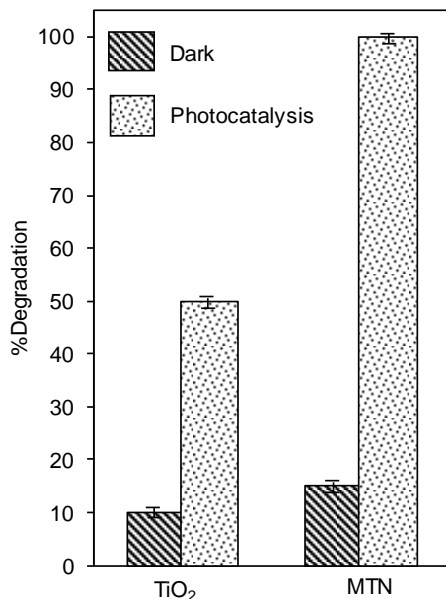


Fig. 4 Adsorption and photocatalytic performance of TiO₂ and MTN for degradation of 2-CP [$C_{2-CP} = 10$ mg/L, pH=5, W= 0.0375 g/L, t=5 h, T= 30°C].

important role in the degradation. Herein, the degradation rates of 2-CP were also studied using the Langmuir-Hinshelwood (L-H) model [11] for MTN.

Fig. 5 shows the linear plot of $\ln(C_0/C)$ vs. irradiation time for MTN where all the plots can be roughly fitted to a straight line, indicating the photocatalytic degradation followed pseudo-first-order kinetics models [12]. In this model, the reaction arises on the surface can be made as an assumption when the reaction rate is proportional to the fraction of surface which covered by the substrate. The catalyst surface charge is neutral during isoelectric (pH_{ZPC}), however when the surface become positively charged, the organic pollutant with positively structure dependent will not adsorbed on the surface of the catalyst. The presence of competition among hydroxyl group and water on the same active site cannot be ignored [13]. Table 1 showed that the k_{app} decreased with increasing initial concentration illustrating the system was favourable at low concentration [14]. The values of k_r (reaction rate constant) and K_{LH} (adsorption coefficient) of MTN were found to be 0.1010 mg L⁻¹ min⁻¹ and 0.0002 L mg⁻¹, respectively. It was found the value of k_r was greater than K_{LH} , signifying that adsorption of 2-CP was the controlling step of the process [15]. The MTN catalyst underwent five cycles of regeneration to study its stability and reusability after repeated photocatalytic activity. Fig.6 illustrated that the photoactivity of the catalyst remained remarkable with a slight decrease from 100% (1st cycle) to 93% (5th cycle). The decreased in photoactivity probably due to heat exposure during the drying process between the cycle which caused reduction in surface area and surge the aggregation of the catalyst [4]. A comparison study on degradation of various pollutants over mesoporous TiO₂ catalysts was tabulated in Table 2.

Table 1 Percentage degradation at different initial concentration of 2-CP and pseudo-first-order apparent constant values for 2-CP degradation using MTN [W= 0.0375 g/L, t=5 h, T= 30°C].

Initial 2-CP concentration, C_0 (mg/L)	Degradation, (%)	Reaction rate, k_{app} ($\times 10^{-2} \text{ min}^{-1}$)	Initial reaction rate, r_0 (mg/ Lmin)	R^2
10	100	1.62	0.16	0.9973
30	85	0.65	0.20	0.9978
50	77	0.49	0.25	0.9976
70	73	0.13	0.10	0.9930
100	67	0.07	0.07	0.9966

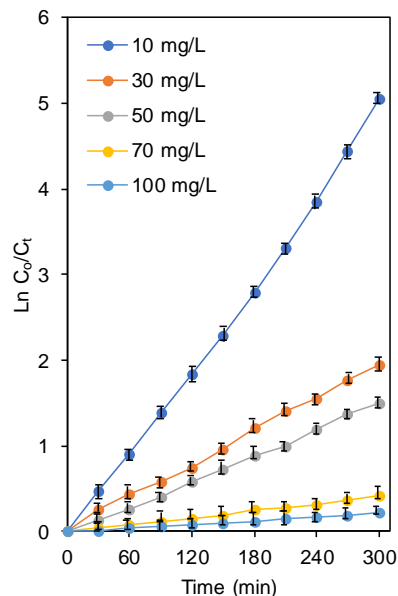
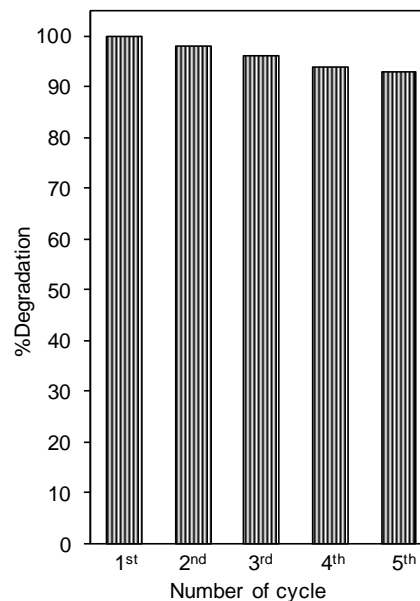

Fig. 5 Photodegradation kinetic of 2-CP using MTN at different initial concentration [pH=5, W= 0.0375 g/L, t=5 h, T= 30°C].

Fig. 6 Reusability performance of the catalyst using MTN [$C_{2-CP} = 10 \text{ mg/L}$, pH=5, W= 0.0375 g/L, t=5 h, T= 30°C].

Table 2 Comparison of photocatalytic activity of various pollutants over mesoporous TiO_2 catalysts

Catalyst	Pollutant	Initial concentration (mg/L)	Dosage (g/L)	Time (h)	Degradation (%)	Ref.
Mesoporous TiO_2 nanoparticles	Dichlorophenol-indophenol	21	1	0.07	95.32	[16]
Mesoporous TiO_2 -curcumin nanoparticles	Methylene Blue	5×10^{-5}	1	1.5	90	[17]
Ag/ Mesoporous TiO_2	Indigo carmine	28	1	1	100	[18]
Ag/ Mesoporous TiO_2	Methyl orange	20	0.3	3	97	[19]
MTN	2-chlorophenol	10	0.0375	5	100	This study

4. CONCLUSION

In this study, MTN was successfully synthesised by microwave (MW)-assisted method using 450W as power density. The catalyst was characterized by XRD and UV-

DRS. The XRD results reveal that MTN has higher crystallinity compared with TiO_2 . In contrast, MTN illustrated lower band gap compared with TiO_2 probably due to the existence of TSD and OV as proven in XPS which contributed to the good performance in photoactivity under

visible light. The kinetic study on degradation of 2-CP over the initial concentration range from 10 to 100 mg/L show the k_{app} decreased with increasing initial concentration illustrating the system was favourable at low concentration and the adsorption of 2-CP was the controlling step of the process.

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