

Heterogeneous photocatalytic degradation of monochlorobenzene in water

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Abstract

This investigation evaluated the photocatalytic degradation of monochlorobenzene (MCB) in an aqueous TiO₂ suspension. In accordance with the experimental results, the degradation of MCB was a function of the initial substrate concentration, incident light intensity, and TiO₂ dosage. However, the solution pH had insignificant effect on the degradation efficiency. The heterogeneous photocatalytic degradation of MCB followed the Langmuir–Hinshelwood kinetics. The adsorption coefficient of MCB (K) and the observed degradation rate constant (k) were calculated as 13.4 mM⁻¹ and 0.0054 mM min⁻¹, respectively. In addition, a 0.255 dependency of the initial degradation rate on the light intensity revealed the considerable adverse effect of e⁻–h⁺ pair recombination. Both mineralization and dechlorination occurred during the photocatalytic degradation of MCB. Under the operating condition of initial MCB concentration of 0.1 mM, light intensity of 5.68 μEinstein s⁻¹, TiO₂ dosage of 1.0 g L⁻¹, and solution pH of 7, about 93.7% of MCB was mineralized after 240 min of irradiation. Nevertheless, 64.3% of the stoichiometric amount of Cl⁻ ions was released into the bulk solution. The simulation results derived from the X-ray photoelectron spectroscopy (XPS) analysis was suggested that the interaction between Cl⁻ ions and TiO₂ surface tended to lower the released amount of Cl⁻ ions.

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1. Introduction

Monochlorobenzene (MCB), one of the hydrophobic and volatile organic compounds (VOCs), is known to cause hepatocellular hypertrophy, renal degeneration and inflammation, and testicular degeneration [1]. Accordingly, it is listed by the United States Environmental Protection Agency as a priority pollutant with a maximum contaminant level (MCL) set at 0.1 ppm [2]. However, MCB is widely used in the manufacture of adhesives, paints, polishes, and dyes and often released in wastewater. Due to its toxicity and recalcitrant nature, MCB is resistant to destruction by biological treatment [3]. Physical methods such as carbon adsorption and air stripping are not destructive but only transfer the pollutants from one phase to another. In addition,

conventional chemical methods are not effective when pollutant concentration is low or refractory to the oxidants. Thus, new technologies for MCB remediation must be considered.

Heterogeneous photocatalysis, an alternative to conventional methods, through irradiation of aqueous TiO₂ suspension offers an oxidation capable of pollutant abatement [4–6]. When TiO₂ is irradiated with photons of energy equal to or higher than its band gap, an electron may be excited from the valence band to the conduction band (e⁻) and leaving a hole in the valence band (h⁺), paired e⁻–h⁺ are created. The photoinduced e⁻ and h⁺ within the particle may diffuse to the surface of TiO₂, and then be able to initiate oxidation and reduction reactions at different sites. In aqueous solution, the h⁺ is scavenged by surface hydroxyl groups to produce highly reactive and nonselective hydroxyl radicals (•OH). At the same time, the e⁻ is trapped by oxygen to form superoxide radical anions (O₂•⁻). Both •OH radicals and O₂•⁻ anions are the primary oxidizing species in photocatalytic degradation [7–9]. The •OH radicals are considered to be

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the dominant oxidizing agent contributing to the destruction of organic pollutants [10,11].

The reason for the increased interest in heterogeneous photocatalysis is the fact that photocatalytic degradation takes place under ambient condition, and no other chemicals are required. Furthermore, the process has been reported to yield almost complete mineralization of organic substrates to CO_2 , H_2O , and relevant inorganic ions [12,13]. It was stated that the photocatalytic efficiency of the UV/ TiO_2 process is dependent on many factors, such as photoreactor design, light intensity, organic substrate, solution composition, and photocatalyst surface composition [14,15]. In this study, the UV/ TiO_2 process was adopted to degrade MCB. Operating factors such as initial substrate concentration, light intensity, photocatalyst dosage, and solution pH were investigated. In order to evaluate the extent of mineralization, the changes in the concentration of total organic carbon (TOC) and Cl^- ions of MCB solution were also examined.

2. Materials and methods

2.1. Materials

Analytical grade MCB ($\text{C}_6\text{H}_5\text{Cl}$, MW = 112.56, density = 1.106 g mL^{-1} , water solubility at $25^\circ\text{C} = 494 \text{ mg L}^{-1}$) with a purity of over 99% was obtained from Merck. Powder TiO_2 (P-25, mixed phase, ca. 80% anatase and 20% rutile) with a specific BET surface area of $47.1 \text{ m}^2 \text{ g}^{-1}$ and primary particle size of 20–50 nm was obtained from Degussa Corporation and used as received. Other chemicals used for analysis including acetonitrile, acetic acid, potassium hydrogen phthalate, phosphoric acid, sodium peroxydisulfate, sodium carbonate, sodium bicarbonate, and sulfuric acid were of analytical reagent grade. Deionized water with saturated oxygen was employed throughout this study for solution preparation.

2.2. Experimental apparatus and procedure

Adsorption experiments were carried in 25 mL centrifugal tubes. The MCB solutions of appropriate concentration were put in contact with 0.25 g TiO_2 (10 g L^{-1}) and then shaken in the dark with thermostatic shaker at 120 rpm and 30°C until equilibrium was reached. After adsorption, the TiO_2 particles were separated by centrifugation immediately, followed by filtration through a $0.22 \mu\text{m}$ Millipore filter. All the filtrates were analyzed by HPLC to detect the changes in the MCB concentration.

The irradiation experiments were conducted in a 2.86 L hollow cylindrical photoreactor equipped with a water jacket. A 15 W blacklight lamp (F15T8 BLB, UVP) with maximum emission at 365 nm was linked to a voltage stabilizer and vertically immersed in a quartz tube placed in the central position of the photoreactor. Different light intensities were obtained by carrying out the experiments at different operating voltages. The incident light intensity was measured using potassium ferrioxalate actinometry. Cooling water from a thermostatic bath (TUNGTEC BL-20) was circulated through the photoreactor jacket to ensure that the temperature inside the photoreactor was maintained at 30°C . A magnetic stirrer located at the bottom of

the photoreactor kept the TiO_2 particles suspended during the irradiation.

2.5 L of MCB solution with desired concentration was mixed with required amount of TiO_2 in the photoreactor. The initial pH of solution was adjusted to predetermined levels by the addition of dilute NaOH or HNO_3 solutions. After 30 min of premixing in the dark, photocatalytic degradation was initiated by switching on the UV lamp. At given illumination time intervals, the suspension was sampled. The collected samples were centrifuged, and then filtered through a $0.22 \mu\text{m}$ Millipore filter for further analysis. The separated TiO_2 was characterized by X-ray photoelectron spectroscopy (XPS).

2.3. Analytical methods

The residual MCB was quantified by HPLC (Biotronik HPLC BT 7900) equipped with a Linear UVIS 200 UV detector and an ODS2 C18 column (length 25 cm, inner diameter 4.6 mm). The eluent was composed of acetonitrile (70%), water (29%), and acetic acid (1%). The flow rate was kept at 1.5 mL min^{-1} and the detection wavelength selected for detecting MCB was 265 nm. TOC measurements were carried out using a TOC analyzer (O. I. Analytical Model 700) equipped with a non-dispersive infrared detector (NDIR). The concentration of Cl^- ions accumulated in the solution was determined by Dionex 4500I ionic chromatography equipped with an IonPac AG4A separation column. The eluent was composed of 1.8 mM Na_2CO_3 and 1.7 mM NaHCO_3 and had a flow rate of 2 mL min^{-1} . A 50 mN H_2SO_4 solution was used as regenerent. XPS measurement was performed using a photoelectron spectrometer (Thermo VG-Scientific, Sigma Probe) equipped with an Al $K\alpha$ radiation of 1486.6 eV. All the binding energies (Eb) were referenced to the Ti 2p peak at 456 eV.

3. Results and discussion

3.1. Adsorption of MCB onto TiO_2 surface

Dark adsorption was performed to evaluate the adsorption of MCB onto the TiO_2 surface. For isotherm adsorption, the adsorption capacity of MCB onto TiO_2 surface versus the MCB concentration in equilibrium is presented in Fig. 1. As can be seen, the adsorption data was fitted to the Langmuir isotherm.

$$Q_e = \frac{Q_{\max} K_{\text{ads}} C_e}{1 + K_{\text{ads}} C_e} \quad (1)$$

where Q_e is the amount of MCB adsorbed on the TiO_2 when equilibrium is achieved, Q_{\max} is the theoretical maximum amount of MCB adsorbed onto the TiO_2 surface, C_e is the MCB concentration in equilibrium, and K_{ads} is the adsorption constant. A linear relationship was obtained with reciprocal adsorption capacity and reciprocal equilibrium concentration. The values of Q_{\max} and K_{ads} could be calculated as $7.1 \mu\text{mol g}^{-1}$ and 1.08 mM^{-1} , respectively, from the intercept and slope of the linear regression. The low value revealed that the adsorption of MCB onto TiO_2 surface was weak.

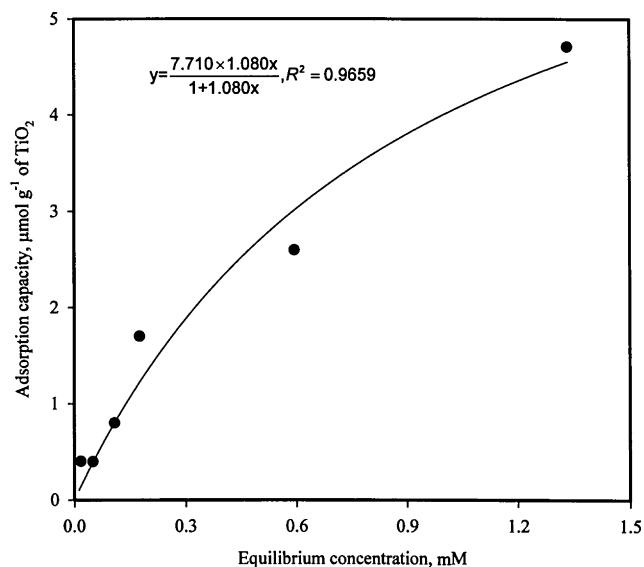


Fig. 1. Adsorption isotherm of MCB onto TiO₂ surface.

3.2. Effect of substrate concentration

The influence of initial substrate concentration on the photocatalytic degradation of MCB is illustrated in Fig. 2. The examined range of the initial MCB concentration was varied from 0.025 to 0.27 mM. As seen in Fig. 2, when the TiO₂ suspension was exposed to UV light, the MCB concentration decreased markedly with illumination time. According to the typical time-dependent MCB concentration, the illumination time for complete destruction increased with increasing initial concentration. For the initial MCB concentration of 0.025 mM, no residual MCB was found after 40 min of irradiation. Additionally, 70 and 180 min of illumination time were needed for complete elimination of initial MCB concentrations of 0.06 and 0.1 mM, respectively. In comparison, for the higher initial

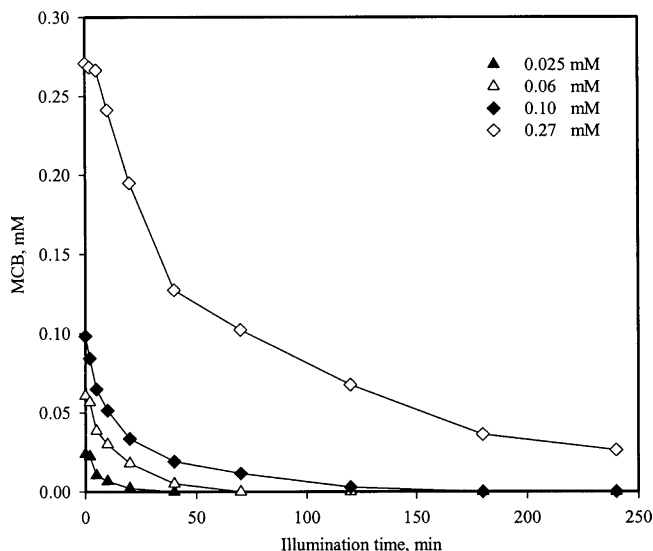


Fig. 2. Effect of initial substrate concentration on the photocatalytic degradation of MCB (light intensity = 5.68 μEinstein s⁻¹; [TiO₂] = 1 g L⁻¹; pH 7).

concentration of 0.27 mM, 9.7% MCB still remained in TiO₂ suspension after 240 min of irradiation.

Numerous investigations have demonstrated that the heterogeneous photocatalysis of organic substrates could be described by the Langmuir–Hinshelwood kinetics [7,16–18]. The kinetic model assumes that the surface coverage of substrate, which in relation to the concentration in the bulk solution, affects the rate of degradation. Applying the Langmuir–Hinshelwood model for the photocatalytic degradation of MCB, the rate equation can be expressed by

$$r_0 = \frac{kKC_0}{1 + KC_0} \quad (2)$$

where r_0 is the initial degradation rate of MCB, C_0 is the initial MCB concentration, k is the observed degradation rate constant, and K is the adsorption coefficient for MCB, respectively. Rearranging Eq. (2) it can be observed that a linear relationship exists between the reciprocal initial rate and the reciprocal initial substrate concentration:

$$\frac{1}{r_0} = \frac{1}{kKC_0} + \frac{1}{k} \quad (3)$$

Fig. 3 shows a double-reciprocal plot of r_0 versus C_0 . A linear regression can be obtained and the calculated value of K and k were 13.4 mM⁻¹ and 0.0054 mM min⁻¹, respectively. In comparison with the adsorption experiment, the value of the calculated adsorption coefficient K for photocatalytic degradation was about 12 times higher than the adsorption constant K_{ads} in the dark. The improvement of the adsorption constant may be ascribed to the additional photoadsorption or the fast photocatalytic reaction under UV irradiation [18].

For dilute aqueous system, the photocatalytic degradation was limited by the amount of substrate available at TiO₂ surface [19,20]. Increasing the concentration of MCB in the bulk solution enhanced the opportunity of MCB to be adsorbed on the TiO₂ surface and acted to promote the initial rate of photo-

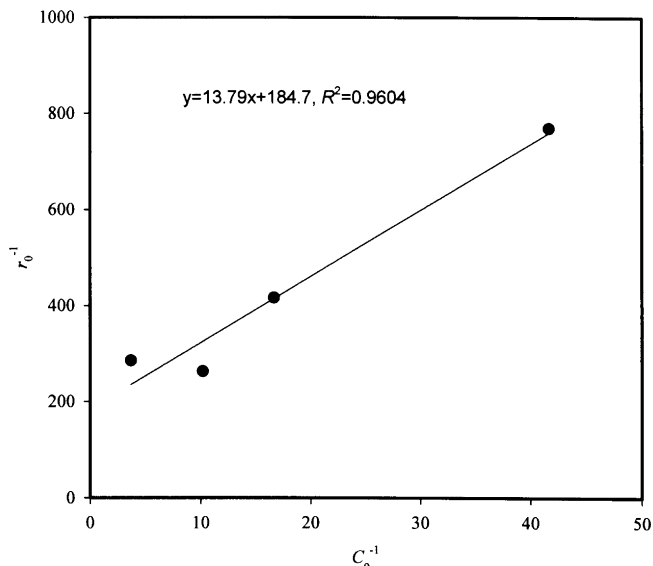


Fig. 3. Linearized reciprocal plot of initial degradation rate as a function of initial MCB concentration.

catalytic degradation. Accordingly, the initial degradation rate increased with increasing initial MCB concentration. Above a certain level, however, the initial degradation rate remained almost constant. This phenomenon may ascribe to that the increase in the initial concentration did not lead to a proportionate increase in the adsorption of MCB onto TiO₂ surface. As a result, the initial degradation rate increased gradually at higher initial MCB concentration. Moreover, owing to the fact that MCB could absorb UV light to initiate direct photolysis [21], excess MCB would lead to a decrease in light penetration. Due to part of the incident light was not used for photocatalytic degradation, the degradation efficiency of MCB was restrained at higher initial MCB concentration.

3.3. Effect of light intensity

The dependence of the photocatalytic degradation of MCB on the incident light intensity was studied in the range from 0.84 to 5.68 $\mu\text{Einstein s}^{-1}$. Fig. 4 illustrates the MCB concentrations as a function of illumination time under four different light intensity irradiations. As can be seen, the degradation efficiency enhanced with increasing incident light intensity.

Modification of the Langmuir–Hinshelwood model was required in order to consider the effect of light intensity [22,23] and Eq. (2) had altered to the form

$$r_0 = \frac{kKI^n C_0}{1 + KC_0} \quad (4)$$

where n is the dependency of the initial degradation rate on the light intensity. Correspondingly, a linear relationship was introduced with logarithmic initial rate and logarithmic light intensity:

$$\ln r_0 = n \ln I + \ln \frac{kKC_0}{1 + KC_0}. \quad (5)$$

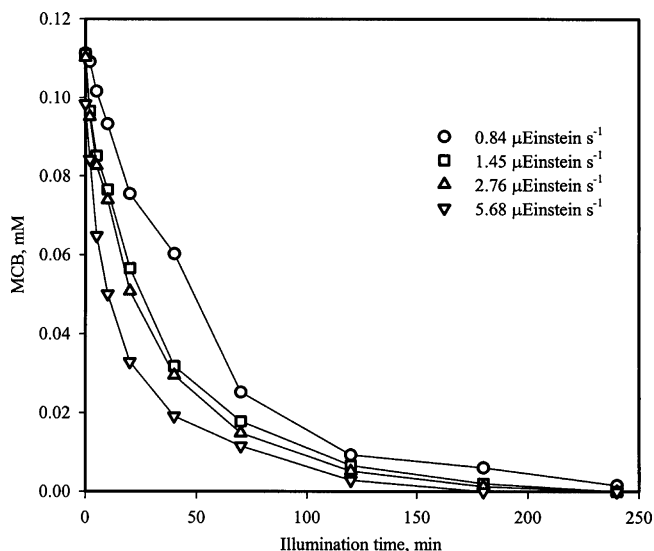


Fig. 4. Effect of light intensity on the photocatalytic degradation of MCB ([MCB] = 0.10 mM; [TiO₂] = 1 g L⁻¹; pH 7).

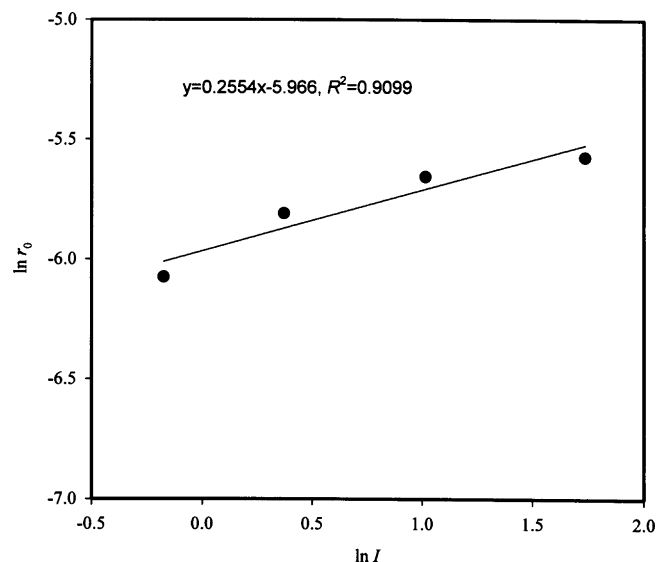


Fig. 5. Linear plot of logarithmic initial degradation rate as a function of logarithmic light intensity.

Fig. 5 shows a plot of $\ln r_0$ against $\ln I$. Linear regression analysis illustrated that the slope was equal to the value of n . The calculated result indicated that a 0.255 dependency of the r_0 on the I existed in the examined intensity range. In addition, the photonic efficiency was 0.050 under 0.84 $\mu\text{Einstein s}^{-1}$ irradiation. However, it decreased to 0.011 when the light intensity increased to 5.68 $\mu\text{Einstein s}^{-1}$, there was thus a reciprocal relationship between the photonic efficiency and light intensity.

It has been well established that the photocatalytic reaction is initiated by the band gap excitation of TiO₂ under UV irradiation, followed by the generation of $\bullet\text{OH}$ radicals. In UV/TiO₂ process, the generation of oxidizing agents depends on a set of two pairs of competing reactions. One is the creation of paired $e^- - h^+$ followed by charge carrier trapping, the other is the recombination of $e^- - h^+$ pairs [24,25]. At low light intensity range, the higher incident light intensity resulted in a greater increase in the probability of absorption between photons and active sites on the TiO₂ surface. The enhancement of degradation rate with increasing light intensity was attributed to there being more light energy to be used for the photocatalytic degradation. Similar observations have been reported in the literature for other model compounds in the analogous light intensity range [26–28]. In addition, it should be noted that the opportunity for the recombination of photoinduced $e^- - h^+$ pairs, which is regarded as an unfavorable reaction, increased with light intensity [27,29]. Consequently, the increment in the initial degradation rate was declined gradually at higher light intensity irradiation. The nonlinear relationship between the initial degradation rate and incident light intensity revealed the opportunity of $e^- - h^+$ pair recombination and radiation energy loss [25,30].

3.4. Effect of photocatalyst dosage

Time courses of MCB concentration as a function of photocatalyst dosage are exhibited in Fig. 6. After the illumination time of 240 min, MCB was almost complete destroyed by

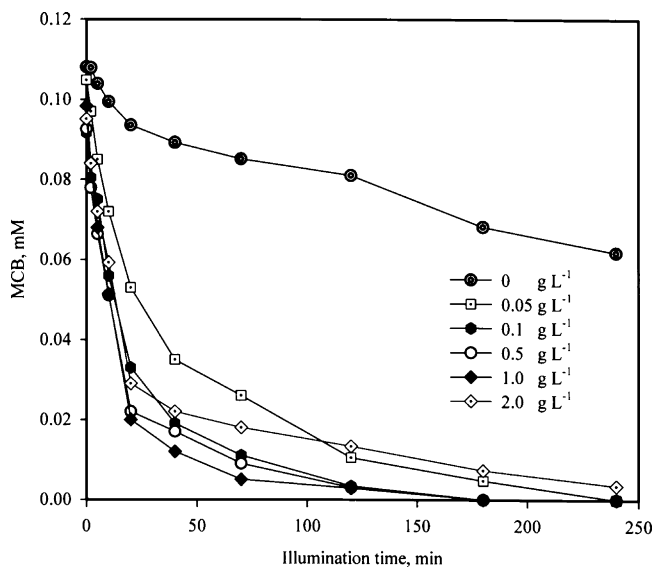


Fig. 6. Effect of photocatalyst dosage on the photocatalytic degradation of MCB ([MCB] = 0.10 mM; light intensity = $5.68 \mu\text{Einstein s}^{-1}$; pH 7).

UV/TiO₂ process in the examined TiO₂ dosage range. This can be compared with approximately 42.8% degradation for the same experiment carried out in the absence of TiO₂. The difference between direct photolysis and UV/TiO₂ process implied that UV light and TiO₂ together had an obvious effect on the degradation of MCB. As shown in Fig. 7, an additional rate enhancement of 6.3 times was achieved at 1.0 g L^{-1} TiO₂ compared with the direct photolysis.

From Fig. 7, the r_0 generally increased with the increase of the photocatalyst dosage, up to 1.0 g L^{-1} . However, at higher dosage (2.0 g L^{-1}), the r_0 was lower than those of other dosage. The influence of photocatalyst dosage on the degradation of MCB can be explained in terms of the active sites on the TiO₂ surface available for photocatalytic degradation and the penetration of UV light into the TiO₂ suspension. As the dosage of photocatalyst was increased, an increase in the active surface area of TiO₂

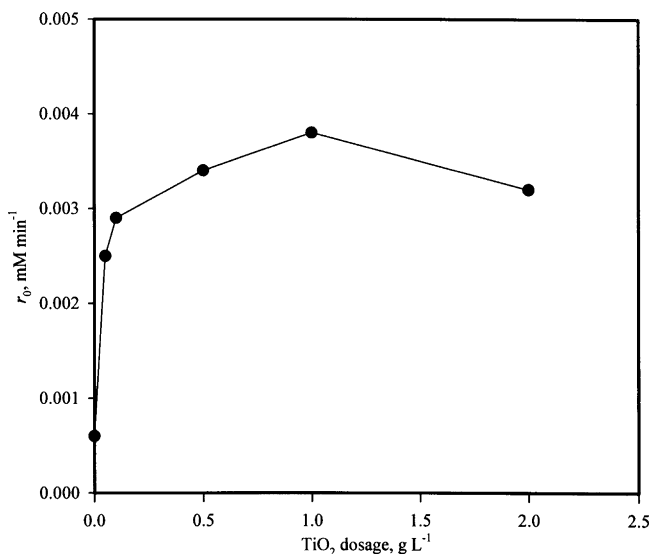


Fig. 7. The initial degradation rate as a function of photocatalyst dosage.

was obtained. The enlarged amount of photons absorbed and the amount of MCB adsorbed on the TiO₂ surface promoted the photocatalytic degradation. When the TiO₂ dosage was overdose, however, owing to an increase in the turbidity of the TiO₂ suspension, a shielding effect of excess particles occurred. Due to the decline of light penetration, TiO₂ particles far from the light source could not be efficiently excited [24,31]. Since not all the TiO₂ surface would be accessible for the MCB degradation, there was an upper plateau observed for the r_0 when the photocatalyst dosage was high. Moreover, the shrinking of the photoactivated volume of the suspension resulted in a reduced performance. In this study, the optimum photocatalyst dosage was 1.0 g L^{-1} , similar to that observed by other researchers [7,32,33].

3.5. Effect of solution pH

The role of solution pH in the photocatalytic degradation of MCB was investigated under the determined experimental condition with initial MCB concentration of 0.1 mM, light intensity of $5.68 \mu\text{Einstein s}^{-1}$, and TiO₂ dosage of 1.0 g L^{-1} . The variations of MCB concentration for a variety solution pH in the range of 3–11 during photocatalytic degradation are presented in Fig. 8. Referring to Fig. 9, the kinetic results indicated that the r_0 was increased from 0.0031 to 0.0038 mM min^{-1} when the solution pH increased from 3 to 7. Nevertheless, the r_0 decreased from 0.0038 to 0.0029 mM min^{-1} at higher solution pH.

It was suggested that the effect of solution pH on the photocatalytic degradation is a complex subject associated with the reaction mechanism and the adsorption characteristics of substrate onto TiO₂ surface [12,34,35]. According to the principle of heterogeneous photocatalysis, the concentration of OH⁻ ions is critical for the generation of •OH radicals [17,36]. Thus, raising the pH of solution was proposed to enhance the number of OH⁻ ions on the TiO₂ surface and promote the photocatalytic degradation. Nevertheless, it should be noted that the lifetime of •OH radicals is very short, photocatalytic reactions can only

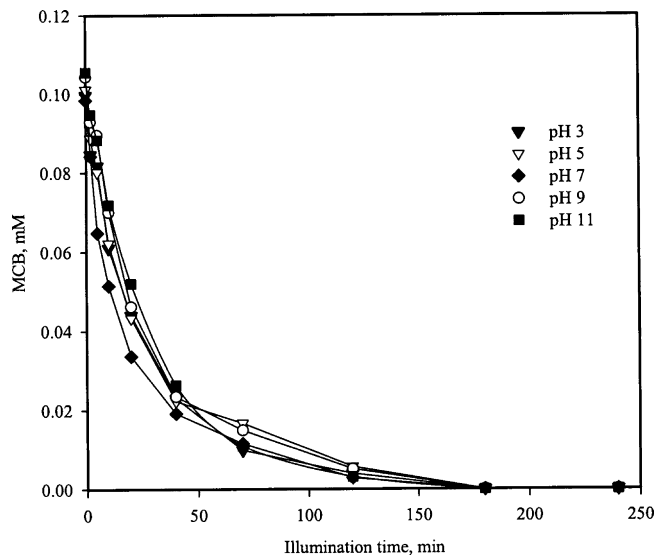


Fig. 8. Effect of solution pH on the photocatalytic degradation of MCB ([MCB] = 0.10 mM; light intensity = $5.68 \mu\text{Einstein s}^{-1}$; [TiO₂] = 1 g L^{-1}).

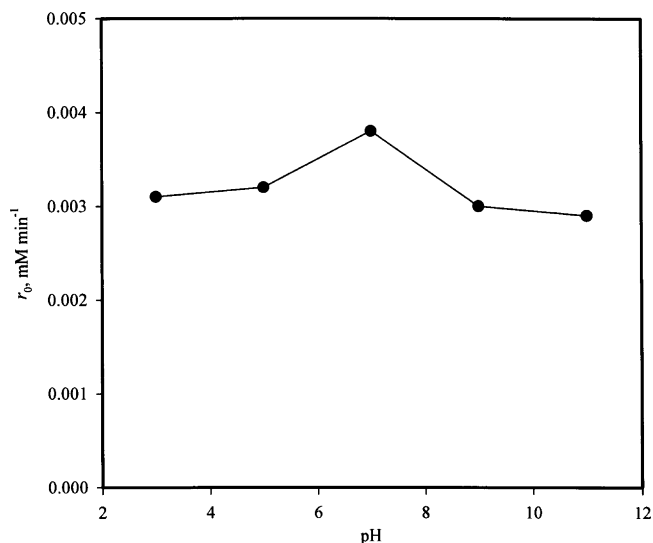


Fig. 9. The initial degradation rate as a function of solution pH.

take place at or near the surface of TiO_2 [19,37–39]. For Degussa P-25, the zero point charge (pH_{zpc}) is about 6.25 [40]. This means that the TiO_2 surface would be positively charged in an acidic solution, negatively charged in an alkaline medium, and neutral when the transition solution pH value is around 6.25. Due to the non-ionic property of MCB, the neutral TiO_2 surface seems beneficial for the adsorption of MCB. Considering the combined effect of the generation of OH radicals and the interaction between MCB and the surface of TiO_2 , the photocatalytic degradation of MCB was most efficient in neutral medium.

3.6. Mineralization of MCB

The evaluation of the MCB mineralization was performed under the following experimental condition: MCB concentration of 0.1 mM, light intensity of $5.68 \mu\text{Einstein s}^{-1}$, TiO_2 dosage of 1.0 g L^{-1} , and solution pH of 7. The concentrations of MCB, TOC, and Cl^- ions during photocatalytic degradation are illustrated in Fig. 10. From the typical temporal file shown in Fig. 10, it can be seen that the concentration of TOC decreased with illumination time as the MCB decayed. The extent of TOC decay was about 93.7% after 240 min of irradiation. Notably, it was found that complete destruction of MCB occurred within 180 min irradiation. The phenomenon illustrated that the mineralization efficiency was less than the degradation efficiency. The difference between the mineralization and the degradation process implied that there were transient organic intermediates present in the photocatalytic system. Therefore, prolonged illumination time would be reasonable for complete mineralization.

It was suggested that the photocatalytic degradation of MCB started with the attachment of $\bullet\text{OH}$ radicals to aromatic ring bringing about C–Cl bond cleaving [32,41]. Accordingly, the dechlorination happened along with the degradation of MCB, and the Cl atom of MCB was released into the bulk solution in the form of Cl^- ions. As can be seen in Fig. 10, the Cl^- ions accumulated markedly with illumination time to reach a maximum concentration value of 0.064 mM. The increase in the

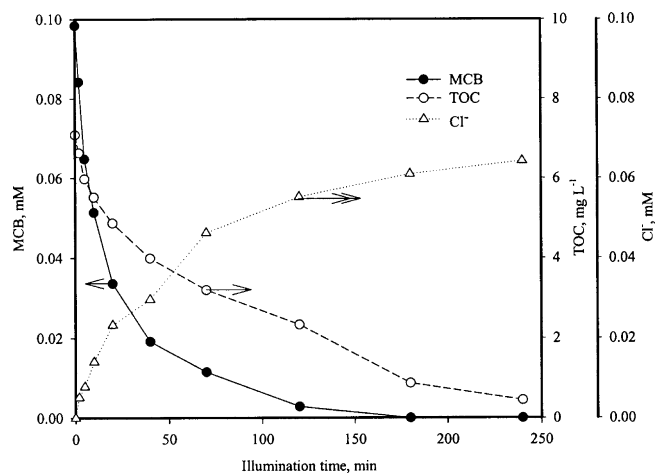


Fig. 10. Variations of MCB, TOC, and Cl^- ion concentration vs. illumination time during photocatalytic degradation of MCB ($[\text{MCB}] = 0.10 \text{ mM}$; light intensity = $5.68 \mu\text{Einstein s}^{-1}$; $[\text{TiO}_2] = 1 \text{ g L}^{-1}$; pH 7).

Cl^- ion concentration was in compliance with the decline in the MCB concentration. Nevertheless, the quantity of Cl^- ions released was approximately 64.3% of the stoichiometric amount after all MCB in the TiO_2 suspension was degraded.

The lower concentration of Cl^- ions than the predicted theoretical value could be ascribed to two reasons. One is that chlorine-containing intermediates such as chlorophenol, chlorocatechol, and chlorohydroquinone, etc. [42,43] may produced from MCB via react with $\bullet\text{OH}$ radicals. The other is that Cl^- ions was adsorbed on the TiO_2 surface instead of being released into the bulk solution. This is an important consideration bearing in mind that the chlorine-containing intermediates could undergo further degraded. According to the experimental results shown in Fig. 10, the ratio of Cl^- ions released was less than the mineralized ratio of TOC which implied that the latter reason may be the major one.

3.7. Characteristics of TiO_2

After photocatalytic degradation, the chemical composition of TiO_2 surface was characterized by XPS. As shown in Fig. 11(a), the elements of Ti, O, and C were detected. The XPS spectrum indicated that Ti and O were the major elements on the surface. Since the peak for C was reflect in the sample stage, the signal can be treated as background noise. Fig. 11(b) shows an enlargement of the XPS pattern in the binding energy range from 450 to 470 eV. A comparison with fresh TiO_2 shows that the binding energy value of the Ti 2p transferred to a lower value. The shift in Ti 2p binding energy could be due to the changes in the chemical status of Ti. The results of fitting the high-resolution XPS spectrum with database are listed in Table 1.

Table 1
Peak fitting results of the high-resolution XPS spectrum of Ti 2p

Chemical status	Eb (eV)	Area ratio
TiO_2	459.2	0.58
TiCl_4	458.5	1

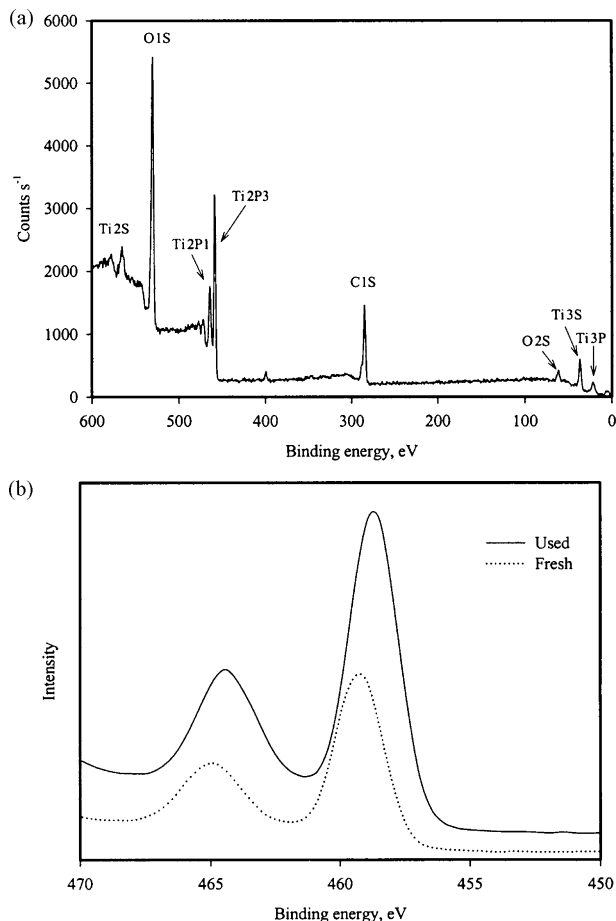


Fig. 11. (a) XPS spectrum for the surface of TiO_2 after photocatalytic degradation of MCB. (b) Comparison of the Ti 2p peak of the fresh and used TiO_2 .

The calculated results revealed that the peak of Ti 2p was composed of two species. The main contributions was ascribed to TiCl_4 (Eb at 458.5 eV), and the other to TiO_2 (Eb at 459.2 eV). The appearance of TiCl_4 suggested that the chemical status of Ti has been changed through interaction with Cl^- ions during photocatalytic degradation of MCB. This phenomenon implied that the Cl^- ions were likely to substitute the O atom and then bond with Ti atom. Accordingly, the simulation value of TiCl_4 was larger than that of TiO_2 at the particle surface. In addition, the reaction between Cl^- ions and TiO_2 surface resulted in the concentration of Cl^- ions in bulk solution being lower than the theoretical value.

4. Conclusions

Heterogeneous photocatalysis using TiO_2 as photocatalyst was proven to be an effective method for the degradation and mineralization of MCB. The experimental results demonstrated that increasing the substrate concentration, light intensity, and TiO_2 dosage in an appropriate range contributed to the photocatalytic degradation of MCB. Additionally, the neutral medium was beneficial for the degradation of MCB. The photocatalytic degradation of MCB followed the Langmuir–Hinshelwood kinetics. Moreover, the initial degradation rate varied with a

0.255 power of the light intensity indicated the considerable adverse effect of e^- – h^+ pair recombination. A comparison of the typical time-dependent MCB and TOC concentrations suggested the production of transient intermediates. An analysis of Cl^- ion concentration in the bulk solution and the characteristics of TiO_2 concluded that the Cl^- ions reacted with TiO_2 particles consequently making the amount of Cl^- ions released lower than theoretical value.

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