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Linuron decomposition in aqueous semiconductor suspension under visible light irradiation with and without H_2O_2

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ABSTRACT

The degradation of LNR in TiO_2 suspension with and without H_2O_2 was investigated under the irradiation of visible light at 419 nm. The removal of LNR in TiO_2-P25 suspension can be increased from 10% to nearly 100% by simply adding H_2O_2 to the process after 3 h of reaction. Various types of TiO_2 including anatase, rutile and TiO_2-P25 exhibited different photocatalytic activities on LNR decay, while their performances were strongly dependent on the presence and/or absence of H_2O_2. The performance of using other metal oxides (semiconductors) as alternatives for TiO_2 was also studied. Among three selected semiconductor oxides, ZnO was found to be most effective for the reaction without H_2O_2, while significant rate enhancement was observed for TiO_2-P25 and WO_3 as H_2O_2 was used.

The H_2O_2-assisted TiO_2 photocatalysis using visible light could be optimized by adjusting TiO_2 dosage, initial concentration of H_2O_2 and the initial pH of the system. The LNR decay rate, generally, increased with the increase of TiO_2 dosage, but too high the TiO_2 was not cost-effective due to the light attenuation. The initial H_2O_2 concentration did not show a significant influence on the reaction rate because the amount of the available electrons on the TiO_2 surface is likely the rate-limiting factor rather than the concentration of H_2O_2. A neutral initial pH level was found to be favorable for the H_2O_2-assisted photocatalysis under visible light, which made the proposed process more attractive for real application.

1. Introduction

Semiconductor-induced photocatalysis has received intensive attention as an environmental remediation technology over the past decades [1–5]. Among all semiconductors, Titanium dioxide (TiO_2) is believed to be one of the most appropriate photocatalysts in terms of environmental application owing to its particularly optical properties, innocuity, low cost and enduring stability regarding photo- and chemical corrosion [6,7]. In general, a photon with energy higher than the bandgap energy (Eg = 3.2 eV and 3.0 eV for anatase and rutile phases, respectively) of TiO_2 can initiate the excitation of electron from the valence band (VB) to the conduction band (CB), leaving a hole, h_{vb}^+ behind [8]. These charged species are believed to induce the generation of free radicals such as $OH^\bullet$ and $O_2^{\bullet-}$ which play a major part coupling with h_{vb}^+ in the oxidation of organic compounds [7]. The widespread use of TiO_2 as an effective photocatalyst, however, has been curbed by its poor light absorption in the visible region due to its large band gap. Therefore, efforts have been devoted to improve the utility of TiO_2 by shifting its optical response from the UV to the visible spectral range. Using transition metal and nonmetal doping to lower the threshold energy for the excitation of electron in the valence band plays a big part in these efforts [9–16]. In addition, recently photosensitization via surface adsorbed organic dyes and coordination metal complexes also holds promise for extending TiO_2 absorption into the visible region [17–19]. Whereas doping and photosensitization have demonstrated successful performance in either narrowing the band gap of TiO_2 or sensitizing photocatalytic properties of TiO_2 towards visible light irradiation, the preparation process of photocatalyst is time-consuming and expensive, which may hinder the use of TiO_2 in practical applications. In this study, a novel and cost-efficient process was developed to allow the degradation of organic compounds in TiO_2 suspension under visible light irradiation with the assistant of H_2O_2.

The widespread application of herbicides as a regular and effective practice to control weed growth has led to increasing environmental concerns in the past decades because of their low biodegradability and long-term persistence in soil. Most herbicides are diffused into aquatic environment via agricultural runoff or leaching [20], which makes them ubiquitous. Linuron (LNR), one of the most important phenylurea herbicides, has received particular attention in recent years due to the toxicity, being frequently detected in the surface and underground waters, and

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possible endocrine disrupting properties of LNR and/or its metabolites [21,22]. Therefore, various treatment techniques have been developed to remove LNR in the aqueous phase, including biological methods [22,23], direct photolysis [24], O_3/H_2O_2 [25], photo-Fenton procedure [21,26], UV/H_2O_2 [27], UV/O_3 [28] and photocatalysis under UV irradiation [29]. The information regarding the photocatalytic decay of LNR under visible light, however, is very limited.

In view of these, this study sets out to examine the photocatalytic decomposition of LNR under visible range irradiation with and without H_2O_2. Its objectives are to explore a new and effective approach to utilize visible light to assist the decay of LNR in semiconductor suspension. The performance of the LNR degradation was investigated in this study under different conditions, such as selection of semiconductors, the effects of TiO_2 phase composition, TiO_2 dosage, the concentration of H_2O_2, and initial pH levels.

2. Materials and methods

2.1. Reagents

Linuron (3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea]) (99%) was obtained from SUPELCO. Three different TiO_2 powders used were anatase, rutile (purchased from Shanghai Kexiang Chemical Reagent Company at 98.5% and 98%, respectively), and Degussa P25, The latter containing 80% anatase and 20% rutile was verified and confirmed by X-ray analysis. The analysis of the specific areas of these TiO_2 powders using the Brunauer–Emmett–Teller (BET) isotherms (Micromeritics ASAP 2010) was 11.4, 9.5 and $55.0\,m^2\,g^{-1}$ for rutile, anatase and Degussa P25, respectively. The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å) at a scan rate of 0.05° 2θ/s. The crystal size of anatase and rutile powders estimated from (1 0 1) and (1 1 0) peaks in XRD spectra is 26.95 and 26.53 nm, respectively (XRD spectra are not shown here). The mean diameters of anatase, rutile and P25 powders were measured to be 265.1, 305, and 211.3 nm, respectively by Zeta Plus/Zeta Potential Analyzer (Brookhaven Instruments Corporation). Nanopowder WO_3 and ZnO (<100 nm) were purchased from Aldrich as well. The H_2O_2 (35% in solution) and titanium oxide sulfate hydrate ($TiOSO_4{\cdot}XH_2O$) was purchased from Riedel-deHaën and International Laboratory, respectively. All other chemicals are analytic purity and all solvents are HPLC grade and used without further purification. For pH adjustment, 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used. The water used in the preparation of all solutions was obtained from a Millipore Waters Milli-Q water purification system.

2.2. Procedures and analysis

The photodegradation of LNR was conducted in a Luzchem CCP-4V photochemical reactor controlled by a computer. To ensure a thorough mixing, 150 mL of solution was dispensed into a 300 mL quartz cylinder with mechanical stirring before and during the illumination. Twelve low-pressure mercury lamps at 419 nm (The emission spectra were shown in Fig. 1) were installed in the photoreactor. The diagram of the experimental installation is shown in Fig. 2, in which 1 mL samples were withdrawn at a predetermined interval and were filtered through a 0.2 μm PTFE membrane to keep the particles free from the solution prior to quantification. All experiments were carried out at room temperature (air-conditioned) at 23 °C in duplicate and the error is less than 5.0%.

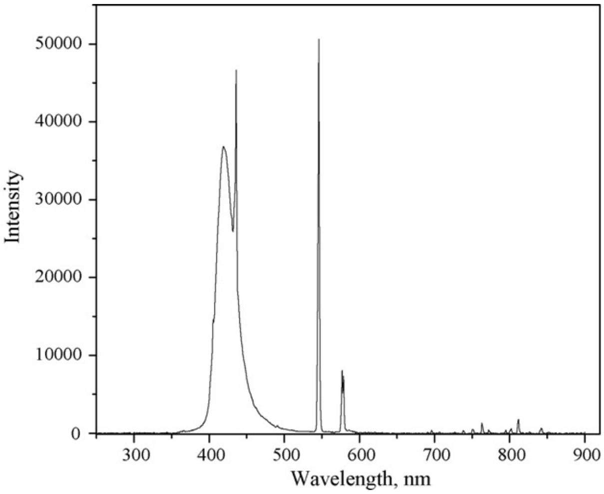

Fig. 1. The emission spectra of 419 nm lamps.

Remaining LNR after photoreaction was determined by HPLC (Waters). The system was comprised of a Waters 515 HPLC pump, Waters 2487 Dual λ Absorbance Detector, an Agilent Hypersil ODS column (5 μm, 0.46 × 25 cm), and Waters 717plus Autosampler. The maximum adsorption wavelength (λ_{max}) was selected as 246 nm for LNR. A mixture of 60% acetonitrile and 40% water was used as the mobile phase running at a flow rate of 1 mL/min. The H_2O_2 concentration was measured by means of UV–visible light absorbance spectroscopy at 408 nm [30]. A Varian CARY 300 UV–visible Spectrophotometer were used to obtain the ultraviolet-visible diffuse reflection spectra (UV–vis DRS) of the samples over a range of 200–800 nm. The emission spectra of lamps were recorded by ILT900 Wideband Rapid Portable Spectroradiometer (International Light Technologies).

3. Results and discussion

3.1. LNR degradation under visible light irradiation in TiO_2–H_2O_2 system

Many studies have shown that, under UV irradiation, H_2O_2 play a dual role in enhancing the semiconductor-sensitized photocatalytic degradation of organic compounds by acting either as an electron scavenger to prevent the recombination of e^- and h^+ or as a direct source of hydroxyl radicals [31–34]. However, under visible light, such information is limited.

In this section, the degradation of LNR was investigated under various conditions including the presence or absence of TiO_2 (P25), the processes with or without H_2O_2, and the use of visible light irradiation or in the dark. As shown in Fig. 3a, it is interesting to observe that the elimination of LNR is insignificant in the systems of

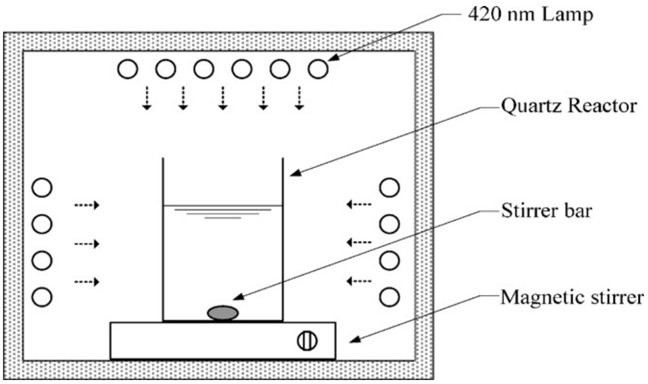

Fig. 2. The diagram of the experimental setup.

$P25/H_2O_2$ (in the dark), Vis/P25 and Vis/H_2O_2 with LNR decay level of 8%, 10% and 8%, respectively, after a 3 h of reaction. However, in the system of $P25/H_2O_2$/Vis, a pronounced enhancement of the reaction rate was observed resulting in a nearly complete decay of LNR.

Though the H_2O_2 itself could not degrade the LNR directly, by using $P25/H_2O_2$ in the dark about 8% of LNR removal was observed. This may result from the TiO_2 surface adsorption and the formation of an oxidizing agent, i.e., a titanium peroxide complex due to the interaction between H_2O_2 and valance-unfilled Ti(IV) on TiO_2 surface [35–37]. It could be verified by both the color change on TiO_2 surface (turned into pale yellow) after the addition of H_2O_2 and the increase of H_2O_2 consumption to 9% comparing to that of 0% when no TiO_2 was involved (Fig. 3b).

The use of visible light irradiation in the presence of P25, however, can slightly increase the LNR degradation to 10%. The upper threshold wavelength that P25 can absorb is 410 nm (data are not shown here), which is within the emission spectra of the 419 nm lamps (Fig. 1) and therefore likely leading to the production of trace amount of e^- and h^+. However, another mechanism that might also contribute to the LNR decay was the surface complexation between organic compounds and TiO_2. It was reported that the formation of complex between the organic compounds harboring function groups such as –OH, –COOH, $-NH_2$ and ≡TiOH groups on the TiO_2 surface might initiate the degradation of organic compound upon absorbing visible light through ligand-to-metal charge transfer [38,39]. An additional test was conducted to verify the latter mechanism by adding 1 M MeOH, a well known hydroxyl radical scavenger, into the reaction and no LNR decay was observed as demonstrated in Fig. 3c. The result suggested that the hydroxyl radical, not the complex, was responsible for the LNR decay.

It was interesting to reveal a synergistic effect in the process of $P25/H_2O_2$/Vis for a quick and complete removal of LNR. The possible explanations for this synergistic effect are: (1) H_2O_2 acts as an electron acceptor to prevent the recombination of e^- and h^+ and/or offering additional hydroxyl radicals (Eq. (1)); (2) The interaction between H_2O_2 and TiO_2 leads to the formation of titanium peroxide complex on the TiO_2 surface which may act as oxidizing species under visible light [36]; (3) Titanium peroxide complex on the TiO_2 surface extend the photoresponse of TiO_2 to the visible region, leading to the generation of the visible light-induced surface electron which can be transferred from surface complexes to the conduction band of TiO_2. The electrons on the conduction band of TiO_2 can then initiate the decomposition of H_2O_2, which gives rise to the generation of hydroxyl radicals (Eq. (2)) [37]; and (4) It was reported that the water-oxide interface can lower the energy barrier for the H_2O_2 decomposition [40]. As a result, additional hydroxyl radicals might be produced by the breakdown of H_2O_2 on the surface of TiO_2 under the irradiation of visible light (Eq. (3)).

$$H_2O_2 + e_{\text{direct}}^- \rightarrow OH^\bullet + OH^- \tag{1}$$

$$H_2O_2 + e_{\text{transfer}}^- \rightarrow OH^\bullet + OH^- \tag{2}$$

$$H_2O_2 + TiO_2 \rightarrow 2OH^\bullet \tag{3}$$

where e_{direct}^- is the electron directly excited from the valence band to the conduction band of TiO_2 and e_{transfer}^- is the electron transferred from surface complexes to the conduction band of TiO_2. The addition of 1 M MeOH significantly inhibits the LNR degradation in this process as shown in Fig. 3c, indicating that the LNR decay

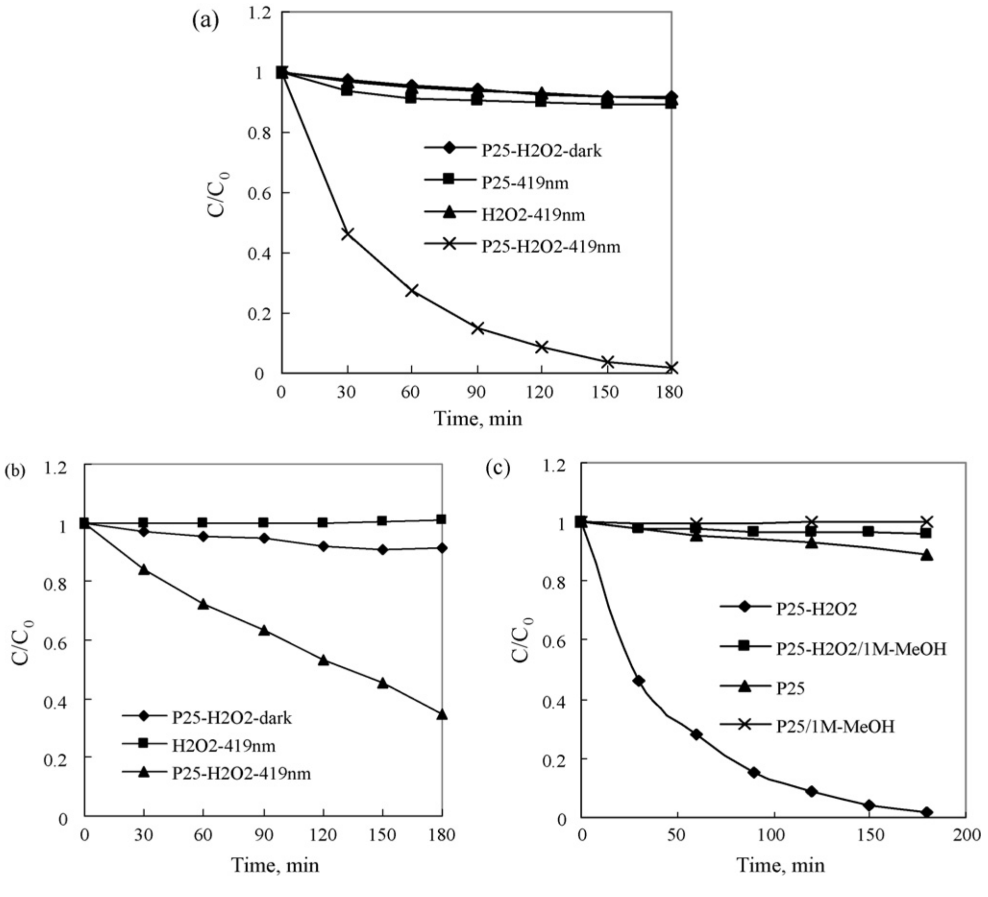

Fig. 3. (a) LNR degradation under different reaction conditions. (b) H_2O_2 decomposition under different reaction conditions. (c) Effect of radical scavenger on visible light photocatalysis of LNR with and without H_2O_2 (Notes: initial LNR concentration is 0.1 mM, TiO_2 loading is 0.6 g/L, the initial concentration of H_2O_2 is 10 mM, initial pH value is 6.0).

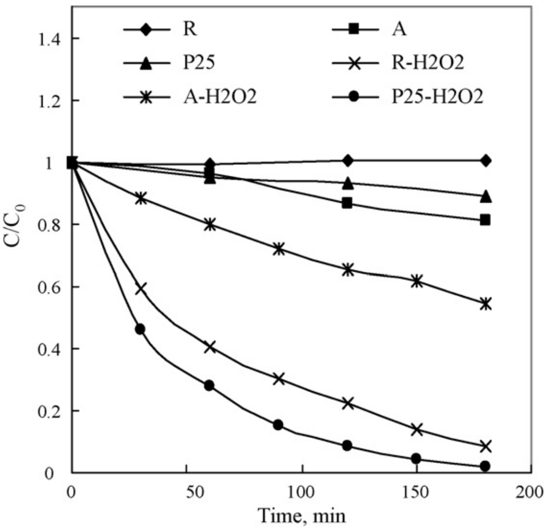

Fig. 4. LNR degradation using different TiO_2 as photocatalysts with and without H_2O_2 (Notes: initial LNR concentration is 0.1 mM, TiO_2 loading is 0.6 g/L, the initial concentration of H_2O_2 is 10 mM, initial pH value is 6.0).

is dominated by various radicals that generated upon the irradiation of visible light while the direct oxidation of titanium peroxide complex may make a trivial contribution to the LNR decay.

The water-oxide interface was reported to lower the energy barrier for the H_2O_2 decomposition and the activation energy was around 42 kJ/mol for the decomposition of H_2O_2 independent of the type of oxide [40]. Thus it may be interesting to examine both the H_2O_2 and LNR decay in the suspension of other metal oxides under the irradiation of visible light. Alumina (Al_2O_3), silica (SiO_2), and gallium oxide (Ga_2O_3), all of which cannot be excited by visible light to produce electron-hole pairs, were selected as probe oxides. However, no H_2O_2 and LNR decomposition was observed in the presence of other oxides except TiO_2 under visible light (data are not shown). This may be because the visible light from twelve 419 nm lamps cannot furnish enough energy (42 kJ/mol) for the cleavage of O–O bond in H_2O_2 to produce hydroxyl radicals.

On the other hand, our previous study confirmed the production of electrons by monitoring the generation of photocurrent in TiO_2/H_2O_2/Vis (visble light) system [41], which substantiate the contribution from the third factor to the generation of hydroxyl radicals. As a result, it is reasonable to believe the first and third factors make major contribution to the degradation of LNR in this system since the second and fourth factors have been ruled out.

3.2. Effect of TiO_2 phase composition

The LNR degradation has been investigated in three different TiO_2 suspensions with or without H_2O_2 under visible light irradiation. Fig. 4 shows that, in the absence of H_2O_2, anatase exhibited the highest reactivity (nearly 20% decomposition of LNR was achieved) and rutile was the worst. However, in the presence of H_2O_2, P25 demonstrated the best performance and followed by rutile and anatase. It is not unexpected that rutile displayed the lowest photocatalytic activity due to its narrow band gap unfavorable for the separation of photo-induced charges [42].

On the contrary, in the presence of H_2O_2, rutile showed a much better performance than anatase. The advantage of rutile in comparison with anatase is that the former can absorb a larger fraction of the emission spectrum of 419 lamps. Rutile powder can absorb photon up to 440 nm while anatase shows absorption only up to 402 nm (data are not shown here). In addition, it was reported that Ti-η^2-peroxide and Ti-μ-peroxide were the dominant bonds to be formed on the surface of rutile and anatase, respectively, in the presence of H_2O_2 [36]. By combining with our previous findings, it's very likely that the Ti-η^2-peroxide has a better performance than the Ti-μ-peroxide in generating free radicals. The P25 demonstrated the best performance when using H_2O_2 as the additional hydroxyl radical source and this is because of its finest particle sizes (or largest surface area) as suggested by many researchers [36,40].

3.3. The performance of different semiconductors under various conditions

Several semiconductors were also examined as alternatives in this study. ZnO has been considered as a suitable replacement to TiO_2 since both are relatively inexpensive and have almost the same band gap energy. While the positive conduction band level of WO_3 (around 0.37 V vs. NHE) might limit its use as a photocatalyst in terms of the oxidative degradation of organic compounds [43], the addition of H_2O_2 to the system may exert a positive effect on the LNR decay by acting as an electron acceptor because the potential for the single-electron reduction of H_2O_2 was reported to be 0.32 V vs. NHE ($H_2O_2 + e \rightarrow OH^- + OH^\bullet$, 0.32 V vs. NHE) [44].

The profile of LNR decomposition in the suspension of the above three semiconductors under a variety of conditions is shown in Fig. 5. It can be seen that purging O_2 led to a significant increase on the reaction rate in all cases. However, the mechanisms for the positive effect which O_2 exerts are different for the three semiconductors. In the case of TiO_2-P25 and ZnO, O_2 acts as an electron acceptor through single-electron reduction to prevent the recombination of photo-induced charges due to their conduction band level (−0.31 V and −0.29 V vs. NHE for ZnO and TiO_2, respectively) [45] more negative than the potential for single-electron reduction of O_2 ($O_2 + e^- = O_2^-$, −0.284 V vs. NHE). In the presence of WO_3, however, the O_2 accepts electrons through multielectron reduction ($O_2 + 2H^+ + 2e^- = H_2O_2$, +0.682 V vs. NHE; $O_2 + 4H^+ + 4e^- = 2H_2O$, +1.23 V vs. NHE) [46]. Fig. 5 also shows the addition of H_2O_2 resulted in a significant improvement on the LNR decay in the cases of P25 and WO_3, while no positive effect was observed for ZnO. This is likely due to the amount of H_2O_2 adsorbed onto the surface of ZnO is negligible in comparison with that in the case of TiO_2 and WO_3 [47,48].

3.4. Effect of TiO_2-P25 dosage

Because TiO_2-P25 has exhibited the best performance comparing to other combinations as described above, it was chosen as the

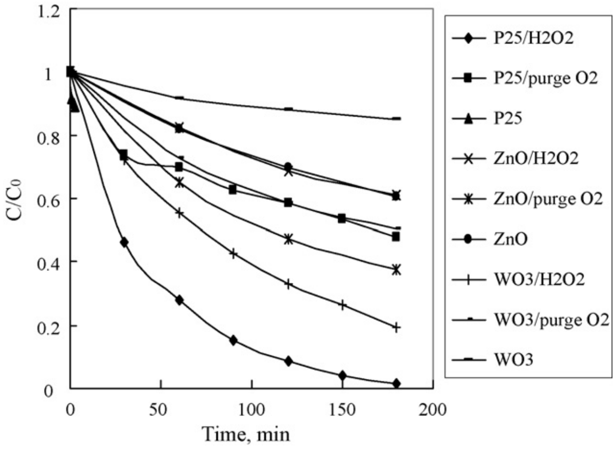

Fig. 5. The performance of various semiconductors under different reaction conditions. (Notes: initial LNR concentration is 0.1 mM, semiconductor loading is 0.6 g/L, the initial concentration of H_2O_2 is 10 mM, initial pH value is 6.0).

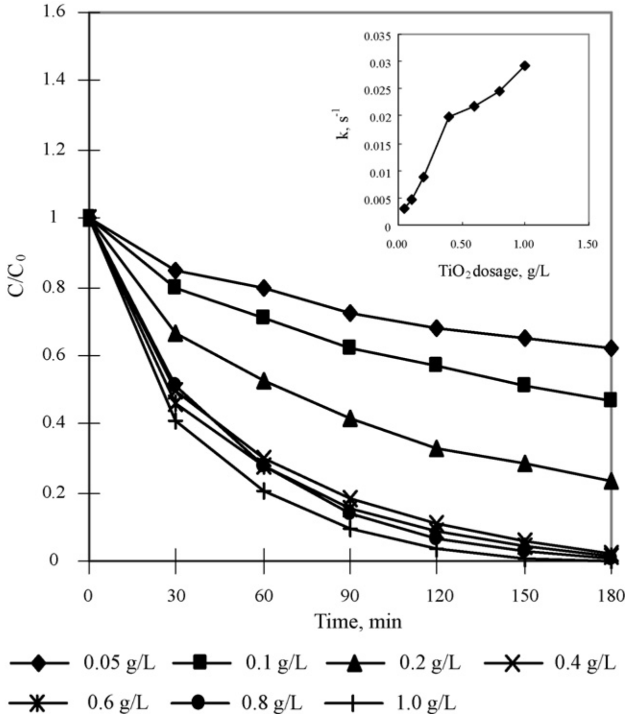

Fig. 6. The effect of TiO_2-P25 dosage on the LNR decay rate (initial LNR concentration is 0.1 mM, the initial concentration of H_2O_2 is 10 mM, initial pH value is 6.0).

exclusive photocatalyst for the detail study. The influence of TiO_2-P25 dosage (ranged from 0.05 to 1.0 g/L) on the LNR degradation was investigated with the concentration of H_2O_2 and LNR fixed at 10 and 0.1 mM, respectively. The decomposition of LNR was found to follow pseudo first-order kinetics at different P25 dosage and the observed rate constants are summarized in Fig. 6, which shows that the decay rate of LNR increases with the increment of TiO_2 dosage. It is also interesting to perceive that the pseudo first-order decay rate constants increased linearly with the increment of TiO_2 dosage, but could be clearly divided into two stages with a breakpoint of 0.4 g/L dosage (the inset of Fig. 6). This suggested that the LNR decay was gradually retarded when TiO_2 dosage was increased over 0.4 g/L. This is because the increase in the opacity of the suspension with the abundance of TiO_2 particles resulted in a reduction in the light penetration [49]. The most cost-efficient dose of 0.4 g/L TiO_2, therefore was employed in the following studies.

3.5. *Effect of H_2O_2 concentration*

As described previously, hydroxyl radicals play a key role in the LNR decomposition in TiO_2/H_2O_2 system under the irradiation of visible light. However, if the H_2O_2 is in excess, H_2O_2 may compete for $OH^\bullet$ with the organic compound (Eq. (4)) and results in a negative effect. The determination of an optimum concentration of H_2O_2, thus, is critical for this system in any practical application.

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \qquad (4)$$

The LNR degradation at 0.4 g/L TiO_2 with H_2O_2 concentration varying from 1 to 20 mM is indicated in Fig. 7. It is interesting to observe that the increase of H_2O_2 concentration did not accelerate the LNR decay significantly, even at the low H_2O_2 concentrations. This result is different from the results by using UV as the light source [32,50]. A possible explanation is that the amount of electrons available in TiO_2/H_2O_2/Vis system is much less than that of the electrons available in UV/TiO2 system, making the amount of the available electrons (but not the H_2O_2 concentration) a rate-limiting factor in the production of hydroxyl radicals.

As also indicated in Fig. 7, the decay rate of LNR with 1 mM H_2O_2 and 2 mM H_2O_2 was retarded after 60 min and 150 min, respectively, which occurred as the H_2O_2 concentration reduced to around 0.1 mM in the solution as shown in Fig. 7b. This indicates that the H_2O_2 concentration might become a rate-limiting factor when it was below 0.1 mM in the solution.

3.6. *Effect of pH level*

The effect of initial pH on LNR decay with the addition of 5 mM H_2O_2 and 0.4 g/L TiO_2 was then examined. The degradation of LNR can be described by pseudo first-order kinetics at different pH levels and the observed rate constants are summarized in Fig. 8a. Under extremely acidic (pH 2.0) and basic conditions (pH 9 and 11), LNR degradation rate was significantly retarded and an optimal pH was found at 6 (see the inset of Fig. 8a). Since H_2O_2, as a dominant resource of hydroxyl radicals, play a major role in this system under visible light, the simultaneous decomposition of H_2O_2 in this system was also examined. Fig. 8b shows the decay of H_2O_2 was noticeably inhibited at pH 2. At pH 2, H_2O_2 exists in the form of $H_3O_2^+$ and TiO_2 carries positive charges since the point of the zero charge (pzc) of TiO_2 is around pH 6. The positive charges on the sur-

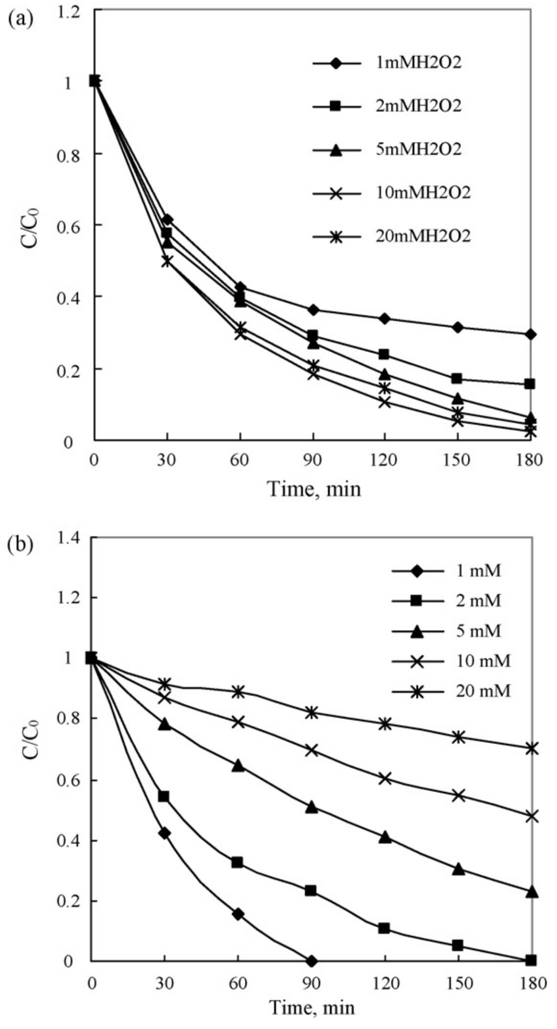

Fig. 7. (a) The effect of H_2O_2 concentration on the LNR degradation. (b) The variation of H_2O_2 concentration during the reaction (Notes: initial LNR concentration is 0.1 mM, TiO_2-P25 dosage is 0.4 g/L, initial pH value is 6.0).

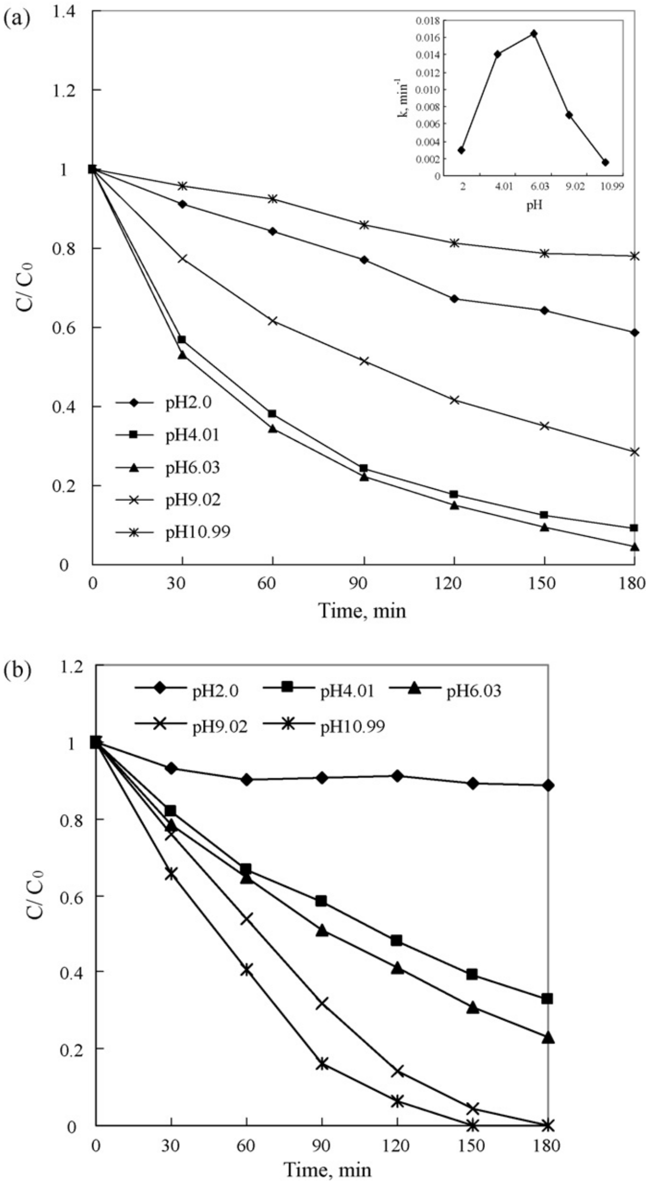

Fig. 8. (a) LNR decomposition at different pH levels (Notes: initial LNR concentration is 0.1 mM, TiO_2-P25 dosage is 0.4 g/L, the initial concentration of H_2O_2 is 5 mM.) (b) H_2O_2 decomposition at different pH levels.

face of TiO_2 may hamper the adsorption of $H_3O_2^+$ on the surface of TiO_2 due to electrostatic repulsion, leading to the retardation of the formation of Titanium peroxide complex and the decomposition of H_2O_2 on the surface of TiO_2. On the other hand, it is well known that H_2O_2 is unstable in an alkaline medium and breaks down rapidly into water and oxygen as demonstrated in Fig. 8b, indicating less H_2O_2 molecules are available for the reactions that can produce hydroxyl radicals. Another minor possible reason for low LNR decay rate under basic condition is the dissolution of CO_2 from the air during the mixing and from the end product of LNR decay. The first and second p*K*a of H_2CO_3 are 6.4 and 10.3, respectively; when the pH level is higher than 6.4, the predominant species of a carbonate system will either be bicarbonate or carbonate ions. Since both of them are radical scavengers, these ions may compete with LNR for hydroxyl radicals [33].

4. Conclusions

The degradation of LNR in TiO_2 suspension with and without H_2O_2 was investigated under the irradiation of visible light. When no H_2O_2 involved, only 10% removal of LNR was observed. However the removal can be significantly increased to nearly 100% upon the addition of H_2O_2 to the process. In the absence of H_2O_2, anatase exhibited higher photocatalytic activities than TiO_2-P25 and no LNR decay was observed in rutile suspension; while in the presence of H_2O_2, TiO_2-P25 demonstrated the best performance and rutile showed higher activities than anatase.

The performance of various semiconductors under varied conditions was also investigated. ZnO showed the highest photocatalytic activities under visible light without using H_2O_2. The addition of H_2O_2 led to a considerable enhancement on the decay rate of LNR in the cases of TiO_2-P25 and WO_3, while no positive effect was observed for ZnO.

The process is optimized by examining the reaction rate under various reaction conditions. The decay rate of LNR, generally, increased with the increment of TiO_2 dosage. However, the LNR degradation could be gradually retarded when TiO_2 was overdosed (above 0.4 g/L) due to the reduction of light penetration.

The H_2O_2 concentration of the tested range (1–20 mM) did not show a significant influence on the LNR decay. This is likely due to the amount of the available electrons on the TiO_2 surface is much less than the H_2O_2 dosage in the solution, the former therefore becomes the rate-limiting factor rather than the concentration of H_2O_2. However, if the initial H_2O_2 is at low end (e.g. 1 or 2 mM) the retardation of LNR decay will be observed as the remaining H_2O_2 in the solution reduced (consumed) to 0.1 mM. The optimal pH level for the H_2O_2-assisted photocatalysis under visible light was found at neutral range, which is beneficial for the purpose of application.

Acknowledgements

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