

Solar-Light-Induced Photocatalytic Degradation of 2-sec-butyl-4,6-dinitrophenol (dinoseb) on TiO₂/MWCNTs Composite Ahotocatalyst

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Abstract: Solar photocatalytic degradation of 2-*sec*-butyl-4,6-dinitrophenol (dinoseb) in aqueous solution by $TiO_2/MWCNTs$ composite particles was investigated. The prepared $TiO_2/MWCNTs$ composite photocatalyst was characterized by XRD, FT-IR, SEM, TEM and UV-vis absorption spectra techniques. The effects of pH, irradiation time, catalyst loading, initial substrate concentration, MWCNTs content and temperature were systematically investigated as operational parameters. The effects of these parameters on the photocatalytic degradation efficiency were found to be significant. Experiment results revealed that the optimal conditions were a dinoseb concentration of 45.3 mg/L at pH 4.30 \pm 0.02 with catalyst loading of 10.0 g/L under solar irradiation for the illumination of 240 min. The highest efficiency on photodegradation of dinoseb can be achieved with an optimal MWCNTs/TiO₂ mass ratio of 0.14%. The photocatalytic degradation of dinoseb followed pseudo-first-order kinetics according to the Langmuir-Hinshelwood model and possible decomposing mechanisms were also discussed. The repeatability of photocatalytic activity was also tested. The photocatalyst was used for seven cycles with photocatalytic degradation efficiency still higher than 95%. The results of the study showed the feasible and potential use of TiO₂/MWCNTs composite in degradation of toxic organic pollutants.

Keywords: TiO₂/MWCNTs composite; Photocatalytic degradation; 2-sec-butyl-4,6-dinitrophenol (dinoseb); Wastewater

1. Introduction

Industrialization and agricultural development, together with population growth, has drastically reduced clean water resources. Alkyl dinitro phenols are widely acknowledged to be a group of toxic refractory chemicals, which can be detrimental to human health and the environment. 2-sec-butyl-4,6-dinitrophenol (dinoseb, CAS No. 88-85-7) is typical example of this class of toxic compounds. Dinoseb is widely used as a herbicide in agriculture for the selective control of grass and broadleaf weeds and as polymerization inhibitor for vinyl aromatics in petrochemical industry [1-2]. A mass of highly toxic nitrophenol waste effluents are generated in the process of dinoseb production. The discharge of this colored dinoseb wastewater in the ecosystem has been problematic due to its toxicity, carcinogenity and resistance to biodegradability. Therefore, the removal of dinoseb from aqueous solution is necessary and very important.

For the removal of recalcitrant dinitrophenols in wastewaters, traditional physical and chemical methods like low-temperature plasma [3], adsorption method [4], sonolysis [5], solar- and UV-assisted Fenton processes

or hydrogen peroxide photolysis [6] have been applied. The main disadvantages of these processes are that they imply transfer the pollutant from one phase to another or convert it to the toxic or carcinogenic compounds [7]. Recently, new oxidation methods called advanced oxidation processes (AOPs) have been widely investigated. Among them, special attention is given to heterogeneous photocatalysis using TiO₂ as a photocatalyst due to its non-toxic, insoluble, inexpensive and highly reactive nature. However, owing to the larger energy band gap of 3.2 eV, normal anatase TiO₂ needs a UV irradiation to initiate its photoactivity, which would greatly hinder the commercialization of TiO₂ photocatalysis. Nowadays, the method of moving the absorption spectrum of TiO₂ into the main part of solar spectrum are widely investigated. It has been found that doping non-metal atoms such as nitrogen, sulfur, carbon, fluorine and boron is one of the most efficient methods to narrow band gap of TiO₂ and shift its optical response to the visible light region [8-12].

Considering the unique electrical properties and high chemical stability of multi-walled carbon nanotubes (MWCNTs), it is expected that the combination of MWCNTs with TiO_2 may induce charge transfer and thus improve the photocatalytic activity of TiO_2 . In our

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earlier research [13], we found that incorporation of MWCNTs into TiO₂ creates a possibility to obtain visible light active photocatalysts. The addition of MWCNTs can remarkably improve the photocatalytic activity of TiO₂ in the degradation of 2,4-dinitrophenol (DNP) under solar irradiation. The aim of the present was the investigation of the photocatalytic activity of the TiO₂/MWCNTs composite prepared by the modified acid-catalyzed sol-gel method which has been reported in our previous work for the degradation of dinoseb in aqueous solution under solar irradiation. The key factors affecting the dinoseb photodegradation efficiency were investigated thoroughly. The photocatalytic activity of TiO₂/MWCNTs composite was compared with that of pure anatase TiO₂ and the possible mechanism relevant to the interaction between TiO2/MWCNTs composite and dinoseb pollutant was also discussed on the basis of the corresponding experimental results.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) were provided by the State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China. Titanium tetrabutoxide (AR, 98% purity) was obtained from Federal Reagent Co. Ltd., Shenyang, China. Dinoseb was used as an alkyl dinitro phenol pollutant and obtained from TaiRui Fine Chemical Co. Ltd., Tianjin, China. Other chemicals including NaOH (1×10^{-2} M), H₂SO₄ (1×10^{-2} M), anhydrous ethanol, acetic acid and nitric acid (67%) employed in this work were AR grade from Tianjin Kermel Chemical reagent Co. Ltd., China. A stock solution of dinoseb (45.3 mg/L) was prepared in double distilled water. Further solutions of different concentrations were made using the same stock solution.

The pure anatase-type TiO_2 and $TiO_2/MWCNTs$ composite catalysts were prepared using a modified acid-catalyzed sol-gel method. The obtained photocatalysts were ground in agate mortar before use. A detailed description of the preparation procedure can be found in [13]. All experiments were carried out with use of double distilled water.

2.2. Catalyst Characterization

The phases and crystallite sizes of the prepared samples were characterized by X-ray diffraction (XRD), performed on a Shimadzu XRD-6000 diffractometer (Japan) at room temperature. The patterns were recorded over the angular range 3-80° (2 θ), using a scan rate of 4.8° 2 θ /min and Cu K α radiation with working voltage and current of 40 kV and 30 mA, respectively. The nature of crystalline phrases present in the prepared composite was checked using database of the JCPDS-ICDD, PCPDF WIN Version 2.02. The surface morphologies of the prepared samples were investigated using High-



resolution Transmission Electron Microscopy (HRTEM, FEI TECNAI G220 S-TWIN Model). The FT-IR spectra of the samples were recorded on a Nicolet Avatar 360 spectrophotometer using conventional KBr pellets. Light absorption properties were measured by a UV-1201 model UV-vis spectrophotometer with a wavelength range of 200-850 nm.

2.3. Photodegradation experiments

Photodegradation experiments under solar irradiation were carried out under similar conditions from 9:30 AM to 2:30 PM on sunny days of March-April 2010 in Dalian, China. The variation in the solar light intensity in a day between 9:30 AM to 2:30 PM were recorded with a PC-2 model radiometer. All experiments were conducted isothermally with a CHS-10A super constant temperature water trough if no special requirement was involved.

A series of capped conical borosilicate flasks charged with 250 mL of aqueous solution/suspension were used as photochemical reactor. The solution/suspension was magnetically stirred. In a typical experiment the photoreactor was loaded with 150 mL of 45.3 mg/L dinoseb aqueous solution and 1.5 g photocatalyst under stirring. The suspension was magnetically stirred for 60 min in the dark to ensure complete equilibration of adsorptiondesorption of dinoseb on the photocatalyst surface. After that period of time, the photoreactor was placed on a fixed support facing south with continuously stirring in order to maximize the contact and absorption of solar radiation. Samples periodically drawn from the photoreactor were centrifuged immediately at 2,000 rpm for 10 min to remove suspended particles and then subjected to analysis. The concentration of dinoseb during the photocatalytic degradation reaction was determined with a UV-vis spectrophotometer from the absorbance at the wavelength of 375 nm by using a calibration curve at pH > 8.0 [14]. The pH value of the solution was adjusted to the desired levels with NaOH or H₂SO₄. Repetition tests were made under the same conditions to ensure reproducibility.

The percentage of degradation was calculated by using the equation given below:

Degradatio n(%) =
$$\frac{C_{\circ} - C}{C_{\circ}} \times 100$$
 (1)

In which C_0 is the initial dinoseb concentration and C is the dinoseb concentration after the treatments.

3. Results and discussion

3.1. Characterization

XRD was used to investigate the phase structure and the phase composition of TiO_2 catalysts. Fig.1 shows the XRD patterns of pure TiO_2 and $TiO_2/MWCNTs$ samples. As shown in Fig.1, all of the samples consist of anatase



as a unique phase (JCPDS, No. 21-1227). The peaks at scattering angles of 25.28°, 37.80°, 48.05°, 55.06° and 62.69° correspond to the reflections from the (101), (004), (200), (211) and (204) crystal planes, respectively. The XRD pattern of the TiO₂/MWCNTs composite contains the same characteristic peaks as that of pure anatase-type TiO₂ but with a lower intensity, which indicated that the addition of MWCNTs can decrease the crystallinity of TiO₂. The peaks of carbon in the pattern could not be recognized clearly because of its amorphous structure and trivial amount of addition.

The structure of TiO₂/MWCNTs composite containing 0.14 wt% MWCNTs is clearly displayed on its TEM image in Fig.2. It can be observed from Fig.2 that TiO₂/MWCNTs particles appear an agglomerated status and almost irregularly sphericity. The aggregated phenomena may be due to sol-gel treatment conditions and the high surface energy of the particles. The irregular shape of the TiO₂/MWCNTs particles can result in light multiple diffusions which may enhance photon utilization efficiency. The pretreated MWCNTs could not be detected by TEM due to its trivial amount of addition.

Fig.3 shows the FT-IR spectra of pure TiO_2 and $TiO_2/MWCNTs$ composite particles. FT-IR spectra of $TiO_2/MWCNTs$ composite and pure TiO_2 showed a similar shape. The absorption peaks at 3420 cm⁻¹ and 1630 cm⁻¹ were attributed to the O-H group. The peak due to stretching and binding modes of Ti-O and O-Ti-O appears around 500 cm⁻¹. The peak at 500 cm⁻¹ in $TiO_2/MWCNTs$ composite spectrum is sharper than that of pure TiO_2 , which may be attributed to the changing of size and crystallinity. The characteristic peak of TiO_2 at 484 cm⁻¹ was so wide that it could hide the finger peak in $TiO_2/MWCNTs$ composite.

The UV-vis absorption spectra of synthesized TiO₂/MWCNTs composite and pure TiO₂ are shown in Fig.4. An obvious red shift of UV-vis spectra of TiO₂/MWCNTs composite was observed when compared with the spectrum of pure anatase TiO₂. Compared with pure anatase TiO₂, the absorption of the TiO₂/MWCNTs is conspicuously intense below 400 nm, while in the visible region the absorption increases remarkably. This suggests that the TiO₂/MWCNTs composite nanoparticles could be excited to produce more hole (h^+_{vb})-electron (e^-_{cb}) pairs than the pure anatase TiO₂ nanoparticles under solar irradiation, which could result in a positive effect on the photocatalytic activity.

3.2. Photocatalytic degradation of dinoseb

3.2.1. Effect of pH

The role of pH on the photocatalytic degradation efficiency was studied in the pH range 1.1-13.0. The results are presented in Fig.5(a). It could be seen that dinoseb can be photocatalytically degraded more efficient at lower pH values. The photodegradation efficiency exhibits a maximum at pH 4.5. At this pH, almost 99.9% of dinoseb was decomposed after 240 min solar irradiation. As can clearly be seen in Fig.5(b), the characteristic absorbance band for dinoseb at 375 nm in the visible region progressively disappeared upon solar irradiation indicating the decomposition of dinoseb was taking place.



Fig.1. XRD patterns of (a) TiO₂ and (b) TiO₂/MWCNTs.



Fig.2. The TEM image of TiO₂/MWCNTs particles



Fig.3. FT-IR spectra of (a) TiO₂ and (b) TiO₂/MWCNTs.





Fig.4. UV-vis absorption spectra of (a) TiO₂ and (b) TiO₂/MWCNTs

Strong acid or alkali is not available for decomposing dinoseb, it is due to the fact that the hydroxyl radical formation reactions are influenced by pH value in solution [15-16]. Besides, the change in solution pH affects the TiO₂ surface ionic speciation. The zero point of charge (pH_{ZPC}) of TiO₂ has been reported as 6.5 [17]. Hence, the TiO₂ surface is positively charged at more acidic pH values, while it is negatively charged at pH values above pH_{ZPC}. The model compound contains OH group and hence they can be protonated and deprotonated under acidic and basic conditions, respectively, depending upon the pK_a value. The pK_a value of dinoseb is reported as 4.62 [14]. Since dinoseb is found to degrade efficiently under acidic pH, the results indicate that this structural orientation is favorable for the attack of the reactive species.

3.2.2. Effect of catalyst loading

Photocatalytic degradation of dinoseb was carried out under optimized conditions with various amount of catalyst (1.2-12.0 g/L) in order to understand their influence in the degradation efficiency. The effect of catalyst loading on the degradation efficiency is shown in Fig.6. As seen, the optimum catalyst concentration for degradation of dinoseb is 10.0 g/L. It is observed that degradation efficiency increases with increase in catalyst concentration from 1.2 to 10.0 g/L, beyond which it levels off. Within the range of catalyst loading from 1.2 to 10.0 g/L, the observed enhancement in degradation may be due to an increased number of available adsorption and catalytic sites on the surface of TiO₂/MWCNTs catalyst. A further increase in catalyst concentration, however, may cause the aggregation of TiO₂/MWCNTs particles resulting in a decrease in the number of surface active sites and increase in opacity and light scattering of suspended particles to decrease in the passage of irradiation through the sample.



Fig.5. (a) Effect of pH on the degradation% of dinoseb and (b) Time dependent UV-vis absorbance spectra of dinoseb: C_0 =45.3 mg/L, catalyst loading = 10.0 g/L, t = 240 min.



Fig.6. Effect of catalyst loading on the degradation% of dinoseb: $C_0 = 45.3 \text{ mg/L}$, pH 4.30 ± 0.02, t = 240 min.

3.2.3. Effect of irradiation time

Fig.7 shows the change of the residual dinoseb with the irradiation time under the optimized experimental conditions. The experimental results clearly show that the dark adsorption and soalr-light-induced photocatalytic degradation of dinoseb without catalyst was negli-



gible. The TiO₂/MWCNTs composite can achieve almost 100% dinoseb removal under sunlight irradiation for the illumination of 240 min, while the degree of degradation of dinoseb by the pure TiO₂ was only about 60% for the same irradiation time. The results indicate that the addition of MWCNTs can enhance the photoactivity of TiO₂ remarkably. For the pure TiO₂ or TiO₂/MWCNTs composite, the removal ratio increases with time, up to 240 min, and, thereafter, it changes slightly. This indicates that photocatalytic degradation of dinoseb with catalysts for 240 min is the optimum irradiation time.



Fig.7. Effect of irradiation time on the photocatalytic performance of photocatalysts: $C_0 = 45.3 \text{ mg/L}$, pH 4.30 ± 0.02, catalyst loading = 10.0 g/L.

3.2.4. Effect of initial concentration of dinoseb

The effect of initial concentration of dinoseb on the rate of degradation of dinoseb was investigated by varying the initial concentration from 11.6 to 45.3 mg/L in the presence of 10.0 g/L TiO₂/MWCNTs catalyst under solar light illumination. Fig.8(a) shows that the removal of dinoseb decreases as the initial concentration of dinoseb increases under solar light illumination. As the initial concentration of the dinoseb increases, the interaction of hydroxyl radical (HO•) with dinoseb decreases. Further, increase in concentration also reduces the light penetration and the relative formation of hydroxyl radicals HO• and super oxide radical anions $O_2^{\bullet-}$ decreases leading to the decreased photo degradation efficiency.

Photocatalytic degradation reactions on TiO_2 surface usually can be expressed by the Langmuir-Hinshelwood model:

$$-\frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{k_{\mathrm{r}}K_{\mathrm{ad}}[C]}{1+K_{\mathrm{ad}}[C]}$$
(2)

where k_r is the rate constant and K_{ad} is the adsorption equilibrium constant. The dinoseb molecules are adsorbed onto the TiO₂/MWCNTs surface and the adsorption-desorption equilibrium is reached in 60 min. After adsorption the equilibrium concentration of the dinoseb solution is determined and it is taken as the initial concentration for kinetic study. Since the adsorption is relatively weak, Eq. (2) can be simplified as follows:

$$-\frac{d[C]}{dt} = k_r K_{ad}[C] = K[C]$$
(3)

In which *K* represents the apparent reaction rate constant. Integrates Eq. (3), yielding

$$\ln\left[\frac{C_0}{C}\right] = K t \tag{4}$$

Plotting ln (C_0/C) versus reaction time t yields a straight line, and the slope is the apparent rate constant K(Fig.8(b)). The obtained K confirms that the photocatalytic reaction approximately follows the pseudo-firstorder kinetics with K from 2.38×10^{-2} to 1.28×10^{-2} min⁻¹ in the dinoseb concentration range of 11.6-45.3 mg/L. The results showed that an increase in the initial concentration of dinoseb leads to a decrease in the apparent rate constant K. A possible reason is the intermediate products may compete with the dinoseb molecules for the limited adsorption and active sites on the surface of the catalyst, and hence inhibit the degradation rate to a certain extent. Another possible reason is the dinoseb molecules may absorb a significant amount of light at high concentration rather than the catalyst and this may also reduce the catalytic efficiency.



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Fig.8. (a) Photocatalytic degradation of dinoseb at various initial concentrations(C_0) using TiO₂/MWCNTs and (b) Relationship between $\ln(C_0/C)$ and reaction time of dinoseb photocatalytic degradation

3.2.5. Effect of MWCNTs content

Fig.9 shows dependence of photocatalytic reaction rate constant K on the MWCNTs content of TiO₂/MWCNTs composite. It can be seen from the figure that the apparent rate constant increases gradually at a region of MWCNTs content below 0.14%, but then decreases. The highest rate constant was observed for the sample, which contained 0.14% MWCNTs. The photoactivity of TiO₂/MWCNTs composite was not proportional to the content of MWCNTs and 0.14 % of MWCNTs with respect to TiO₂ in composite was the best condition to achieve the synergism between TiO₂ and MWCNTs. An appropriate MWCNTs content can possible accelerate the production of h^+_{vb} -e⁻_{cb} pairs. The effect of charge separation induced by MWCNTs is not obvious when the MWCNTs content is low. When the MWCNTs content increases remarkably, guite a number of MWCNTs would surround some active sites of TiO₂ and thus hinder the contact between TiO₂ and oxygen contained species, which may result in the decrease of photocatalytic activities.



Fig.9. Relationship between $ln(C_0/C)$ and reaction time of dinoseb photocatalytic degradation with TiO₂/MWCNTs particles synthesized with different MWCNTs/TiO₂ mass ratio

3.2.6. Reuse of TiO₂/MWCNTs catalyst

The repetitive use is very important for the practical application of $TiO_2/MWCNTs$ photocatalyst, due to the fact that its use for longer period of time leads to a significant cost reduction of the treatment. For this reason, the catalyst was recycled seven times and the catalysis efficiency of the $TiO_2/MWCNTs$ composite photocatalyst was still higher than 95% after be used for 7 cycles. This indicates that the photocatalytic activity of $TiO_2/MWCNTs$ has repeatability. The reduction in the degradation percentages among the cycles may be explained by the formation of intermediates and their accumulation in the cavities and on the active surface sites of the catalyst. Also, catalyst aggregation during the

catalytic process can decrease part of the catalyst surface for both photo absorption and dinoseb adsorption.

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3.2.7. Postulated mechanism

The postulated mechanism of photocatalytic degradation of dinoseb in the presence of TiO₂/MWCNTs composite under solar light irradiation was proposed (Fig.10). MWCNTs as adsorbent and conductive material can absorb the solar light irradiation and transfer the photogenerated electron (e_{cb}) into the conduction band of TiO₂ particles efficiently. When TiO₂/MWCNTs composite is illuminated with the solar light, electrons are promoted from the valence band via MWCNTs to the conduction band of the semi conducting oxide to produce $h^+_{vb}-e^-_{cb}$ pairs. This electron transfer between MWCNTs and TiO₂ semiconductor enhanced the photocatalytic activity of the composite. The h_{vb}^+ potential is positive enough to generate hydroxyl radicals at the surface and the e_{cb} potential is negative enough to reduce molecular oxygen. With this understanding, the role played by MWCNTs can be illustrated by injecting electrons into TiO₂ conduction band under visible light illumination and triggering the formation of very reactive radicals super-oxide radial ion (O2 -) and hydroxyl radical (HO[•]), which were responsible for the degradation of dinoseb.



Fig.10. Plausible photocatalytic mechanism of $\rm TiO_2/MWCNTs$ under solar irradiation.

4. Conclusions

In this study, photocatalytic degradation of a typical alkyl dinitro phenol, 2-*sec*-butyl-4,6-dinitrophenol (dinoseb), was investigated by the use of TiO₂/MWCNTs composite catalyst. The TiO₂/MWCNTs composite can cause an obvious red shift of UV-vis spectra compared with pure anatase TiO₂. The observations also clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high degradation efficiency. The optimal conditions for the photocatalytic degradation of dinoseb were determined to be: initial concentration of dinoseb, 45.3 mg/L; pH value, 4.30 ± 0.02 ; catalyst loading, 10.0 g/L; irradiation time, 240 min. An optimal MWCNTs/TiO₂ mass ratio of 0.14



% was found to achieve the highest efficiency on photodegradation of dinoseb. Further kinetic studies reveal that the photocatalytic degradation of dinoseb followed pseudo-first order kinetics with respect to dinoseb concentration. No obvious decline in efficiency of the composite photocatalyst was observed after 7 repeated cycles and this made the application of the TiO₂/MWCNTs catalysts for degrading toxic organic pollutants from aqueous solution under solar irradiation more practical.

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