



Photocatalytic degradation of 2,4-dinitrophenol

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ARTICLE INFO

Article history:

Received 17 December 2007

Received in revised form 31 July 2008

Accepted 6 August 2008

Available online 27 August 2008

Keywords:

Photocatalysis

Phenol

Degradation

Titanium dioxide

ABSTRACT

Contamination of the food supply from agricultural waste is an increasing concern worldwide. Numerous hazardous chemicals enter the environment from various industrial sources daily. Many of these pollutants, including 2,4-dinitrophenol (2,4-DNP), are water soluble, toxic, and not easily biodegradable. The solar photocatalytic degradation of 2,4-DNP was investigated in a solution of titanium dioxide (TiO₂) that was prepared to be an optically clear aqueous solution of nanosized particles of TiO₂. In order to achieve optimal efficiency of the photodegradation, the effects of light intensity and pH were conducted. All experiments were carried out in a batch mode. At a pH of 8, maximum removal of 70% of 2,4-DNP was achieved within 7 h of irradiation time. The nearly homogeneous solution of 5.8 nm TiO₂ particles, size determined by XDS, were very effective in the photocatalytic degradation of 2,4-DNP.

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1. Introduction

The world's most precious natural resource – water – is being threatened by numerous contaminants, resulting in a water contamination crisis with both local and national implications [1–3]. Several conventional methods of water treatment exist including filtration, chemical precipitation, ion exchange adsorption, electro deposition, and membrane systems and as such they have found certain practical applications. They are, however, either slow or non-destructive for some or more persistent organic pollutants. The need to remove highly toxic compounds from potential sources of drinking water with efficient catalytic materials is very important [4–6]. Thermal catalysts have been intensely investigated for this purpose, however, the reaction rates of such systems are slow compared to those possible with photoactivation. An advantage of photocatalysts is their reactivity at various temperatures, whereas thermal catalysts typically require high temperature for operation. In addition, light-activated catalysts can be easily turned “on” or “off” in the presence or absence of a photon source, respectively. More efficient photocatalysts that operate with visible light are necessary to improve cost efficiency, to utilize solar energy, and to avoid the formation of highly toxic side products. Photocatalysis with titanium dioxide as catalyst under UV irradiation has proven to be an

efficient method to completely mineralize organic compounds [7–10].

Nitrophenols are common components of industrial effluents and have been detected in urban and agricultural waste. 2,4-Dinitrophenol (2,4-DNP) is the most important of the six possible dinitrophenol forms. The commercial product Triolit, a wood preservative, contains 80% NaF, 5% Na₂Cl₂O₇ and 15% 2,4-DNP. 2,4-DNP is used in the manufacture of pesticides. It is also used in the production of 2,4-diaminophenol which is used in the medical treatment of obesity. 2,4-DNP is also used as an intermediate to make dyes, photochemical, and explosives and as an indicator for the detection of potassium and ammonium ions. It may enter the environment from industrial discharges, spills, or possibly as a breakdown product of certain pesticides containing 2,4-DNP moieties. 2,4-DNP exists as a yellowish crystalline solid, is soluble in water (5.6 g L⁻¹ at 18 °C), and is volatile with steam. It has strong acid properties with a pK_a value of 4.03. In the natural environment, phenol derivatives are toxic and refractory pollutants. Moreover, phenols are only partly biodegradable and, therefore, they are not easily removed in biological wastewater treatment plants [11–14]. The time needed for these chemicals to disappear chemically in air is not known. They break down (degrade) in water and surface soil, but the breakdown takes longer at lower soil depths and groundwater. Therefore, they are expected to stay longer in the deep soil of dump sites compared to surface soil and may even stay indefinitely in these soils. That is why there is a need to develop effective methods for the degradation of these pollutants, either to less harmful compounds or to their complete mineralization.

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1.1. Solar detoxification—photochemical degradation

Short wavelengths (~295–400 nm) of solar radiation can generate direct and indirect photolytic processes and degrade pesticides and PCBs polluting soil and surface waters. Since short wavelengths are attenuated more strongly than longer visible wavelengths in the atmosphere, the rate of photolysis of pesticides is highly dependent on latitude, season and other meteorological conditions. Thus, in tropical regions, photochemical processes could be a key factor to assess pesticides fate and degradation [15].

Solar energy can be used to degrade hazardous organic chemicals by direct thermal decomposition or by photochemical reaction. Some advantages include savings in fuel use, improved thermal destruction of contaminants, and the reduction of exhaust gas volumes, including products of incomplete combustion (PICs). These processes can use either thermal energy or a range of photochemical reactions. In order to achieve high efficiency to decompose contaminants, the concentration of the radiation is required. This can be achieved by reflecting solar radiation by mirrors (heliostats) and absorbed by a receiver where temperatures of up to 2300 K are reached. High destruction efficiencies can be achieved at temperature much lower than the temperature required for thermal incineration.

In solar detoxification, the main photochemical processes that aid thermal treatment include photocatalytic oxidation using titanium dioxide (TiO_2) as a catalyst. TiO_2 may take on any of the following three crystal structures. Brookite, rutile, which is stable at high temperatures, and anatase which tends to be more stable at low temperatures. Anatase and rutile both have tetragonal crystal structure but the anatase structure has the highest photoactivity.

In photocatalytic reactions ultraviolet radiation is used to promote an oxidation reaction using TiO_2 as catalyst in the presence of oxygen [16]. The reactivity of singlet oxygen, irradiated with visible light in the presence of dissolved oxygen, is used in the dye-sensitizer processes. The reactive species produced can then react with contaminant molecules in the waste. All pesticides can be degraded by OH radical generating agents (such as methylene blue). Each system has different capabilities which need to be taken into consideration when making comparisons [17,18].

2. Experimental

2.1. Chemicals used

Titanium tetrachloride (TiCl_4) in the liquid form and polyvinyl alcohol of molecular weight 13,000–23,000 were obtained from Sigma–Aldrich chemicals, St. Louis, MO. Sodium hydroxide was obtained from Fischer Scientific Company, Fair Lawn, NJ. Dinitrophenol was obtained from Mallinckrodt Chemicals, St. Louis, MO. All chemicals were used without further purification.

2.2. Instrumentation

A low-pressure mercury lamp was obtained from CENCO, central Scientific company, Franklin park, IL (8 W source). A Varian Cary 50, spectrophotometer was employed to measure the UV–vis spectra of the nitrophenol as function of exposure time. A Varian Saturn 2100T, GC/MS was used for analyzing the end degradation products. Determination of pH was made with ORION pH meter Model 420A. A XRD apparatus (a D4 Endeavor Bruker AXS diffractometer operating with $\text{Cu K}\alpha$ radiation source filtered with graphite monochromator, $\lambda = 1.5406 \text{ \AA}$) was used for analysis of laboratory synthesized catalyst solution.

2.3. Sample preparation

2.3.1. Preparation of titanium dioxide suspension

An optically clear suspension of titanium dioxide was prepared by the following method. Deionized water was allowed to sit in an ice bath for 2 h so as to attain a temperature very close to 0°C . In a typical preparation of titania sol, about 1 L of ice cold water containing a magnetic stirrer was placed on a stirring motor. Water was stirred as vigorously as possible and approximately 3 mL TiCl_4 was slowly and carefully added after being withdrawn from the bottle using a syringe. It is important to note that TiCl_4 must be added very slowly, otherwise large particles of TiO_2 forming a white flocculating precipitate. Titanium tetrachloride reacts rapidly with water to form titanium dioxide, TiO_2 . The powder X-ray diffraction analysis of the sample was carried out. The sample was dried and ground to a fine powder using a mortar and a pestle and loaded into the sample holder. The XRD scans were recorded from 10° to $80^\circ 2\theta$ with 0.04° step-width and 10.1 s counting time for every step. The reaction produced TiO_2 with particle size of 5.8 nm UV–vis spectrum of the TiO_2 solution was recorded which showed characteristic absorption edge ~360 nm confirming existence of the TiO_2 in the medium.

2.3.2. Preparation of polyvinyl alcohol–titanium dioxide suspension

Two grams of polyvinyl alcohol were heated in 100 mL of water to produce a homogeneous suspension. An aliquot of 100 mL of Titanium dioxide suspension was added and the mixture was stirred. The pH of the mixture was adjusted with sodium hydroxide solution.

2.3.3. Preparation 2,4-dinitrophenol solution

1.84 g of 2,4-dinitrophenol ($\text{C}_6\text{H}_4(\text{NO})_2$, MW = 184.11) was weighed and dissolved in 1000 mL water. An aliquot of 10 mL of this prepared DNP solution was further diluted to 100 mL with water. And this diluted solution was used for further experiments. The concentration of DNP was measured as a function of time using the UV–vis spectrophotometer.

2.4. Experimental setup

Experiments were carried out in the “dark”, in direct sunlight and with UV radiation. Initial UV–vis spectra of the samples were taken before the start of the experiments. For studies involving exposure to the solar radiation, samples in quartz cuvettes were placed outside before noon (~10 AM). Small aliquot were drawn at predetermined intervals and their UV–vis spectra were recorded to determine the progress of degradation of 2,4-DNP. For exposure to UV radiation, a quartz cuvette containing 2,4-DNP solutions were placed about 6 in. in front of a 8-W UV light source. This geometry was maintained through out the whole series of experiments outlined here. The UV–vis spectra were recorded at fixed intervals (typically 60 min). These results were then compared with the UV–vis spectrum of the unexposed DNP solution to determine the extent of degradation.

3. Results and discussion

Transparent sols of TiO_2 as a photocatalyst were used because (1) the suspension is crystal clear and thus does not block the solar radiation from the solution, (2) the cost of the suspension is low because its concentration is low, (3) TiO_2 absorbs 100% of solar radiation at wavelengths 355 nm and above, and (4) TiO_2 is chemically and thermally inert. In addition, the cost of TiCl_4 , the precursor of TiO_2 , is quite low. Fig. 1 shows spectrum of sample (2,4-dinitrophenol, 5 vol.% TiO_2) at pH 8 at time $t = 0$ min. After 5 h

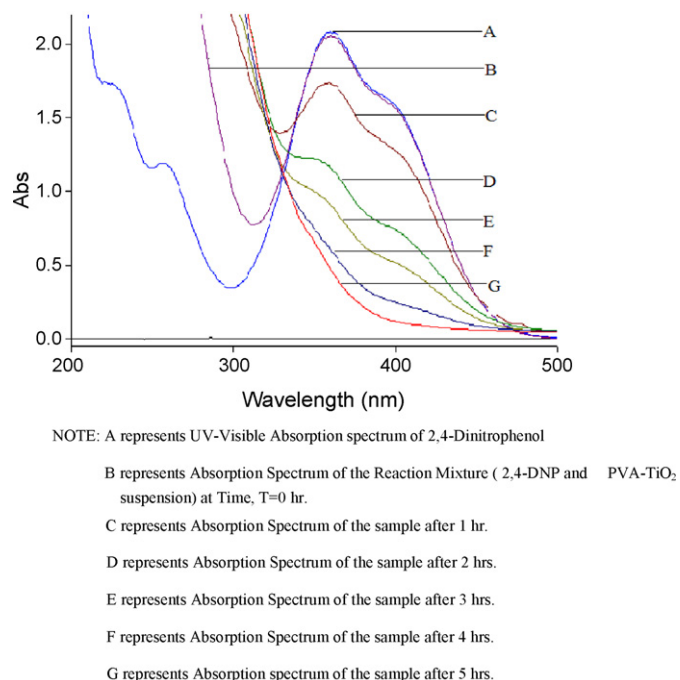


Fig. 1. UV-vis spectra of 2,4-dinitrophenol and PVA-TiO₂ solution (5 vol.%) at pH 8 after 5 h in UV light.

of exposure to UV light, ~45% of 2,4-dinitrophenol was degraded. Fig. 2 shows UV-vis spectrum for the same suspension after 6 h exposure in quartz cuvette. Only 33% of 2,4-dinitrophenol in glass cuvette degraded while for one in the quartz cuvette value was found to be 47%. The difference in degradation efficiencies can be explained by the fact that different materials have different light absorbing capacities. Also, Table 1 shows comparison of degrading efficiencies based on 5 h time cycle.

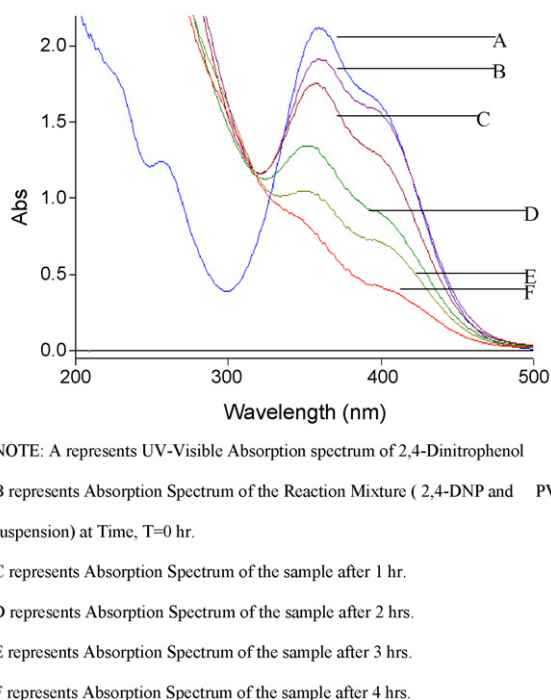


Fig. 2. UV-vis spectrum of 2,4-dinitrophenol and PVA-TiO₂ solution (5 vol.%) at pH 8, in sunlight, after 6 h in Quartz Cuvette.

Table 1
2,4-Dinitrophenol conversion at pH 8 with 5 vol.% PVA-TiO₂ in sunlight

Time (h)	2,4-Dinitrophenol conversion at pH 8	
	Quartz cuvette	Pyrex Glass
1	8.0	4.0
2	14.0	8.0
3	30.67	16.67
5	46.67	33.33

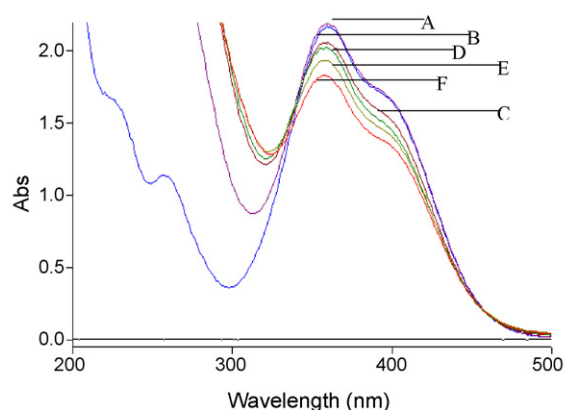


Fig. 3. UV-vis spectrum of 2,4-dinitrophenol and PVA-TiO₂ solution (5 vol.%) at pH 8 after 5 h in laboratory (no sunlight, no UV light).

The experiments that were carried out in the absence of UV light and sunlight (i.e. the sample was kept inside a closed laboratory room) showed that very little degradation occurred as seen in Fig. 3. Only 13% was achieved after 5 h indicating that TiO₂ does not act as a catalyst. Fig. 4 compares the degradation of 2,4-DNP as a function of light source. As shown in this figure, the efficiency of degradation depends on the nature of light. The UV light is more effective than sunlight because it can be controlled. However, sunlight has the advantage of being low tech and low cost. Table 2 shows conversion of 2,4-DNP with different sources of light.

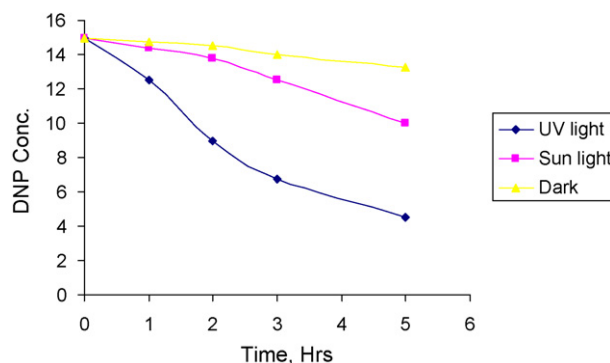


Fig. 4. Effect of light source on 2,4-dinitrophenol degradation.

Table 2
2,4-Dinitrophenol conversion at different sources of light

Time (h)	2,4-DNP conversion at different sources of light		
	UV light	Sun light	Dark
1	16.67	8.0	1.67
2	40.0	14.0	3.33
3	55.0	30.67	6.67
5	70.0	46.67	11.67

A XRD pattern of the laboratory synthesized TiO₂ was obtained to verify that material produced was titanium dioxide and to determine the particle size of the catalyst. XRD results confirmed the substance as the rutile phase of titanium dioxide.

Scherrer's formula for calculation of size of crystallite:

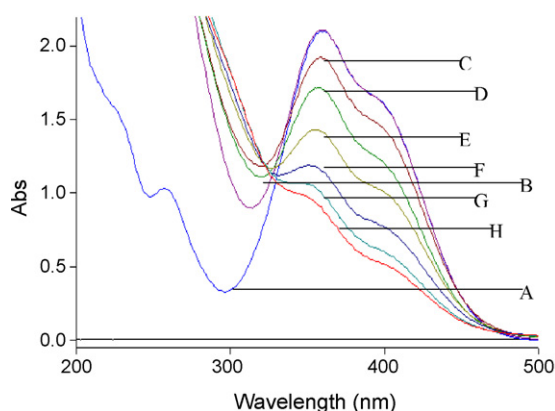
$$\text{size} = k\lambda \times 57.3/B \cos \theta$$

where $k = 0.9$, $\lambda = 1.54 \text{ \AA}$, $\theta = 13.6^\circ$.

Scherrers value for the laboratory synthesized TiO₂ particles was 58 Å or 5.8 nm.

pH is often a major factor influencing the rate of degradation in photocatalytic process. Therefore, experiments were carried out at different values of pH of the PVA-TiO₂ suspension. They were conducted at pH 6–8. Fig. 5 shows spectra at pH 6. At pH of 6, almost 45% of 2,4-DNP was degraded after exposure time of 5 h. At a pH of 7, 45.3% was degraded after 5 h of exposure while at pH 8, the value increased to 70%. At higher pH values of the PVA-TiO₂ suspension, TiO₂ precipitated. Hence pH 8 was found to be optimum at which maximum degradation was achieved. Therefore pH 8 was chosen for all other experiments. Fig. 6 compares the degradation efficiency of 2,4-DNP as function of pH.

In order to determine the end degradation products in the degradation of 2,4-dinitrophenol we have repeated our experiments several times. We have investigated the resulting solution of the



NOTE: A represents UV-Visible Absorption spectrum of 2,4-Dinitrophenol
B represents Absorption Spectrum of the Reaction Mixture (2,4-DNP and PVA-TiO₂ suspension) at Time, T=0 hr.
C represents Absorption Spectrum of the sample after 1 hr.
D represents Absorption Spectrum of the sample after 2 hrs.
E represents Absorption Spectrum of the sample after 3 hrs.
F represents Absorption Spectrum of the sample after 4 hrs.
G represents Absorption spectrum of the sample after 5 hrs.
H represents Absorption spectrum of the sample after 6 hrs

Fig. 5. UV-vis spectrum of 2,4-dinitrophenol and PVA-TiO₂ solution at pH 6 after 7 h in UV light.

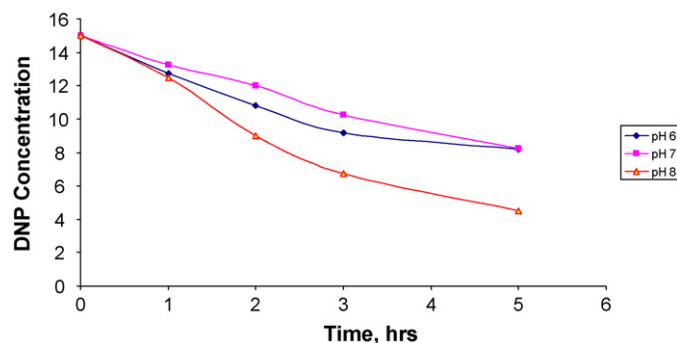
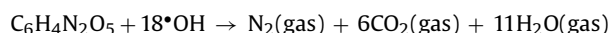


Fig. 6. Effect of pH on 2,4-dinitrophenol degradation.

degradation by UV-vis, GC and GC/MS. In order to substantiate our findings we enlisted the assistance of a local environmental laboratory—Earth Analytical Sciences, Inc., 4825 Ward Dr., Beaumont, TX. Their results of our solution agreed with ours. They showed an 84% reduction of the 2,4-DNP with no other organic compounds present in solution. From our observations it is logical to assume that 2,4-DNP has dissociated into gases products which can possibly be explained by the following reaction:



which is similar to the explosive decompositions of TNT and picric acid.

4. Conclusion

The photocatalytic oxidation of 2-4 DNP is very efficient in sunlight when TiO₂ is used as the catalysis. Other laboratories have utilized TiO₂ in heterogeneous photocatalysis for the degradation of water pollutants as films or powder suspensions [19,20]. The laboratory synthesized 5.8 nm particle size optically clear TiO₂ solution used in this study proved to be more effective from the standpoint of its chemical and photochemical stability. The addition of proper amount of TiO₂ solution to a waste stream could be used to destroy the waste by using solar irradiation. Compared to high capital and operating costs of the common industrial methods to deploy this novel method is very inexpensive and environmental friendly. This method does not add any toxic pollutants. The present investigation shows that photocatalyzed degradation of 2,4 dinitrophenol in sunlight and UV light irradiated clear TiO₂ semiconductor solution can be developed into an alternative dinitrophenol waste treatment. Although TiO₂ absorbs small fraction of solar spectrum, it is still worth considering in industrial process. The lack of any detectable products in the photolyzed solution and the generation of the gas appears to indicate the efficient mineralization of 2,4-DNP to innocuous products by this method. Therefore this appears to be a very attractive method for disposal of nitrophenols and other hazardous materials.

Acknowledgements

The authors wish to thank Eric Postula and Billy Robins with Earth Analytical Sciences, Inc., for the GC/MS analysis. This research was supported by a departmental Welch Foundation Grant V-0004.

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