Photocatalytic Oxidation of 2,4-Dinitrophenol in Aqueous Titanium Dioxide Slurries

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The heterogeneous photocatalytic oxidation of 2,4-dinitrophenol (2,4-DNP) was investigated in aqueous suspensions of TiO₂ at the wavelength of 254 nm by using an annular flow type photo-reactor with an 8W low-pressure mercury lamp as a UV-light source. For achieving higher photo-degradation efficiencies of 2,4-DNP, optimized conditions like, irradiation time, initial concentration of 2,4-dinitrophenol and catalyst load were established. The effect of oxygen supply and the optimum pH for achieving maximum degradation were also investigated. All the experiments were carried out in a batch recirculation mode. Experiments conducted at oxygenated and deoxygenated conditions indicate that the photo-degradation can be carried out through two different mechanisms. Optical density measurement (spectroscopy) was used to study the degradation. At a pH value of 3.5 and 10.5, maximum removal of 99 and 97 per cent was achieved within 3 h of irradiation time with an initial concentration of 4 \times 10^{-3} M.

Keywords: Photocatalytic oxidation, Oxidation, 2,4-Dinitrophenol, Titanium dioxide slurries, Slurries

Introduction

Toxic and hazardous organic compounds are often present in industrial discharges and water supplies. Removal of these compounds may be difficult and expensive, especially if very low concentration levels are to be achieved. These are difficult to degrade by conventional treatment technologies like biological treatment, adsorption over activated carbon, air stripping, and incineration. Use of activated carbon and air stripping are processes based on the phase transfer from aqueous to solid phase and aqueous to gaseous phase, respectively. However the present environmental problems clean and destructive technologies in water treatment, which are away from phase transfer approaches, not only remove contaminants from water but also destroy them in the process. The search for a solution to this problem has involved extensive examinations in the field of advanced oxidation processes (AOPs). AOPs are finding increased application in destruction of water bound organic compounds and employ heterogeneous reactions with photo-reactive metal oxides such as, titanium dioxide, where an irradiated solid semiconductor provides available charges (electrons and positive holes) for the redox transformations of either organic or inorganic contaminants leading to complete mineralisation of the contaminants to carbon dioxide and water ¹.

Photocatalytic reactions of semiconductors such as decomposition of waste pollutants have received special attention in the decomposition of hazardous organic compounds because of their complete mineralization ability and possible application to pollution control using solar energy ²,³ and heterogeneous photo catalysis has recently been claimed to be a promising process for the removal of minute amounts of metal ions in aqueous solutions ⁴,⁵,⁶,⁷,⁸,⁹,¹⁰.

In recent years, a huge increase in the number of studies devoted to photocatalytic abatement of pollutants in aqueous TiO₂ slurry has been recorded ¹¹-¹⁵. The applicability of this technique to the treatment of real wastewaters and process economics has also been extensively discussed ¹⁶,¹⁷.

Several studies on photocatalytic degradation of dyes have been reported ¹⁸-²³. TiO₂ photocatalytic processes are characterized by different interesting
features, the complete mineralisation of the organic compounds being the most important one.

Nitro aromatic compounds are pollutants of considerable concern due to their toxicity and the extent of their use as synthetic intermediates, propellants, and explosives. Commonly found substances include mono-, di-, and tri-nitro substituted benzenes. Oxidative methods for treating wastes containing these compounds are not entirely satisfactory because of the recalcitrant nature of the compounds toward aerobic microbial decomposition and common chemical oxidizing agents. Recently, several studies have appeared indicating that these substances are susceptible to microbial reduction under anaerobic conditions.

Nitro phenols are common components of industrial effluents and have been detected in urban and agricultural waste. 2,4-dinitrophenol is used in the manufacturing of dyestuff intermediates, wood preservatives, pesticides, herbicides, explosives, chemical indicators, photographic developers and also in chemical synthesis, and the effluents in these chemical process industries are likely to contain this hazardous pollutant.

In the present work the photocatalytic oxidation of 2,4-dinitrophenol in aqueous titanium dioxide slurries was investigated at varying reaction conditions like, irradiation period, substrate concentration, TiO2 load, pH to assess the effects of the variables on the degradation efficiency.

**Materials**

2,4-dinitrophenol, AR grade (Aldrich, Germany), TiO2 (80 per cent anatase and 20 per cent rutile) (Degussa P-25) with BET surface area of 50 m2/g (average particle size 30nm) were used. All other chemicals are extra pure grade and were used as received by preparing the solutions in glass double distilled water.

**Reactor Set-up**

The annular-flow photocatalytic reactor used for this study was a cylindrical plastic vessel in which a 8 W low pressure mercury lamp (254 nm), surrounded by a quartz glass tube to protect it from direct contact with an aqueous solution flowing through an annulus between the inner surface of the vessel and the outer surface of the quartz glass tube, located at the axis of the vessel (Figure 1). The study was carried out in a batch recirculation mode. The reactant solution was circulated between the perfectly mixed vessel (1000 mL reservoir) and the annular-flow reactor at a flow rate of 120 mL/min with the peristaltic pump. In all the cases during the photolysis experiments, reactant solution containing the appropriate quantity of the semiconductor powder was continuously stirred before and during illumination and was bubbled with air throughout the reaction process.

**Methodology**

All the experiments were carried at 30 ± 3 °C with an initial pH of 6.8, except for experiments where pH values were varied. The solutions were prepared using double distilled water and pH of the reaction mixture was adjusted, using 0.01N NaOH/H2SO4. In all the experiments, 250 mL of 2,4-DNP solution of appropriate concentration was taken into the reservoir. At specific time intervals suitable aliquots of the sample were withdrawn and analyzed after centrifugation (Remi Research R-24) at 8000 rpm, followed by filtration with 0.20 μm (Mdi, India), Nylon-66 membrane syringe filters.

**Analytical Methods**

The Analysis of 2,4-DNP was carried out at 360 nm spectrophotometrically (ECIL GS5703 AT, India). The photodegradation efficiency for each sample was calculated from the expression:
where \( \eta \) is the photodegradation efficiency, \( C_0 \) is the concentration of the compound before illumination, and \( C_1 \) is the concentration of solution after time \( t \).

Results and Discussion

Mechanism of Photodegradation

Photocatalytic degradation of organic compounds occurs on the surface of TiO\(_2\), primarily in trapped holes. \( ^\bullet \)OH and O\(_2\)\(^{-}\) radicals are considered as primary reactive species and O\(_2\) and H\(_2\)O are necessary for photocatalytic degradation. Oxygen adsorbed on the TiO\(_2\) surface prevents the recombination of electron-hole pairs by trapping electrons and super oxide ions are thus formed. \( ^\bullet \)OH radicals are formed from holes reacting with either H\(_2\)O and OH\(^{-}\) adsorbed on the TiO\(_2\) surface. \( ^\bullet \)OH and O\(_2\)\(^{-}\) are also formed from H\(_2\)O.

In this process, H\(_2\)O\(_2\), O\(_2\) and HO\(_2\) which are suitable for trapping electrons and \( ^\bullet \)OH and O\(_2\)\(^{-}\) are the most important oxidants. The oxidizing power of the OH radicals is strong enough to break bonds of the organic molecule adsorbed on the surface of the TiO\(_2\) leading to the formation of CO\(_2 \) and inorganic ions. When the intensity of light was constant, the number of OH and O\(_2\) increased with increase in irradiation period, resulting in complete photodegradation of organic molecules to smaller fragments, like CO\(_2 \) and H\(_2\)O\(^{1}\) (Figure 2).

Effect of Irradiation Period

The 2,4-dinitrophenol degradation in TiO\(_2\) suspension is found to gradually increase with increasing irradiation period (Figure 3a). With an initial concentration of 4 \( \times \) 10\(^{-4} \) M 2,4-DNP and 150 mg/250 mL of TiO\(_2\), the photodegradation efficiency was about 64 per cent after 1 h of irradiation, while after 8 h of irradiation it was about 98 per cent.

Effects of Initial Concentration of the Pollutant

The continuous UV-irradiation of 2,4-dinitrophenol solution containing TiO\(_2\) powder in suspension leads to a gradual decrease of the phenol concentration.

The amount of 2,4-dinitrophenol degraded for different initial phenol concentration ranging from 0.5 \( \times \) 10\(^{-3} \) M to 5 \( \times \) 10\(^{-4} \) M at pH 6.8 (Figure 3b) indicates greater yields of 2,4-dinitrophenol elimination are obtained as the solution is more dilute. For example, a 99 per cent level of phenol degradation is attained after 3 h of UV-irradiation for an initial 0.5 \( \times \) 10\(^{-4} \) phenol solution, while only 68 per cent is photo degraded for an initial 5 \( \times \) 10\(^{-4} \) M phenol solution at the same experimental conditions. The reason for this behaviour is that as the initial concentration of the compound increases, more organic substances are adsorbed on the surface of TiO\(_2\) but the intensity of light and illumination period is constant and O\(_2\)\(^{2-}\) and O\(^{2-}\) radicals formed on the surface of TiO\(_2\) are also constant. Thus the reactive OH and O\(_2\)\(^{2-}\) radicals attacking the compound molecules decrease and simultaneously the photo degradation efficiency also decreases.

Effect of TiO\(_2\) loading

The effect of catalyst loading on the rate of degradation is shown in Figure 3c. The photo...
degradation efficiency increases rapidly with increase in the amount of TiO₂ from 50 mg to 150 mg/250 mL and then decreases on further increase of TiO₂ for compound concentration of $1 \times 10^{-4} \text{M}$ in 2 h irradiation.

The photo-degradation efficiency decreased from 96 to 80 per cent. The increase in the amount of catalyst increases the number of active sites on the TiO₂ surface that in turn increases the number of OH and O₂⁻ radicals. Further increase in catalyst loading beyond 200 mg the degradation rate decreases due to the retardation of the light penetration and may result in the deactivation of activated molecules due to collision with ground state molecules.

**Effect of pH**

The effect of pH on the photodegradation efficiency is shown in Figure 3d. The pH of the suspension containing $4 \times 10^{-4} \text{M}$ 2,4-DNP and 150mg/250mL of catalyst was 3.5. At this pH when it was irradiated for 3 h complete degradation up to 99 per cent was achieved. Even the pH of the suspension was adjusted to 10.5 with 3 h irradiation period the degradation was found to be 97 per cent. The photodegradation of the 2,4-DNP with varying pH values is expected to be influenced by the adsorption processes that take place on the surface of semiconductor particles.

Figure 3—Effect of (a) irradiation period, (b) initial concentration (c) TiO₂ loading, (d) pH (e) Activation on per cent of photo degradation efficiency of 2, 4-DNP.
It can be assumed that during irradiation 2,4-dinitrophenol is oxidized at the semiconductor-electrolyte interface by direct reaction with the photo-generated holes in the TiO₂ particles or by reaction with OH radicals, which are also powerful oxidizing agents. The OH radicals are formed by reaction between the photo-generated holes with the OH ions adsorbed onto the semiconductor particles.

\[
\text{OH}^{\text{ads}} + h^+ \rightarrow \text{OH}^{\text{ads}}
\]

The higher photo-degradation of 2,4-DNP at alkaline conditions may be due to OH. The fact that higher formation of OH radicals from adsorbed OH ions in the alkaline medium.

\[
\text{TiO}_2 + h^+ \rightarrow \text{TiO}_2(h^+, e^-) \\
\text{TiO}_2(h^+, e^-) \rightarrow \text{TiO}_2 + \text{heat} \\
\text{O}_2^{\text{ads}} + e^- \rightarrow \text{O}_2^{\text{ads}} \\
\text{OH}^{\text{ads}} + h^+ \rightarrow \text{OH}^- (\text{ads}) \\
\text{PhOH}^{\text{ads}} + h^+ \rightarrow \text{Products}
\]

This behavior seems to be characteristics for many photocatalytic systems and similar results have been obtained in photo-degradation of other organic compounds.

**Effect of Bubbling of Air and Nitrogen**

The effect of bubbling of air and nitrogen through the aqueous suspension containing the concentration of \(4 \times 10^{-4} \text{ M}\) 2,4-DNP solution with 150 mg/250 mL of catalyst for 8 h irradiation period on the photo degradation efficiency is shown in Figure 3e. Considerable photo-degradation is found both in oxygenated and deoxygenated conditions. The following mechanisms may be operative in the photocatalytic degradation of 2,4-DNP (Figure 4).

**Conclusions**

The photodegradation efficiency of 2,4-DNP increases with increase in TiO₂ loading up to 150 mg/250 mL. At a pH values of 3.5 and 10.5 maximum removal of 2,4-DNP is achieved. The photodegradation efficiency increased as irradiation period increases, both in the cases of air and nitrogen. The photocatalytic degradation of hazardous toxic pollutant 2,4-DNP with TiO₂ as catalyst under optimized conditions can be exploited for complete minimization and as cleaner technology for hazardous waste treatment.

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**References**

The image contains a chemical diagram illustrating the degradation pathways of 2,4-dinitrophenol (DNP). The pathways are labeled as (1), (2), and (3) and are described as follows:

1. **(1)**: The initial degradation of DNP in the solution phase, involving the abstraction of a hydrogen atom and the formation of a hydroxyl radical, followed by the oxidation of the -NO₂ group.

2. **(2)**: The further oxidation of the intermediates, leading to the formation of CO₂ and H₂O.

3. **(3)**: The degradation of DNP on the surface of a TiO₂ catalyst, showing different reaction pathways leading to the formation of 2,4-dinitrosophenol.

The figure is labeled as Figure 4 — Degradation pathways of 2,4-dinitrophenol.

References:


