



Photodegradation of 2,4,6 trinitrotoluene, nitrobenzene mixtures in TiO₂ suspension

Nguyen Van Chat^a, Do Ngoc Khue^a, Nguyen Van Hung^b, Tran Van Chung^b, I. Francis Cheng^c

^a*Union for Science –Technology of New Products, Hanoi, Vietnam*

^b*Institute of Chemistry and Material, Hanoi, Vietnam*

^c*Department of Chemistry, Univ. of Idaho, Moscow, ID83844, USA*

Abstract

The photo catalytic oxidation of nitrobenzene, 2, 4,6-trinitrotoluene in aqueous suspensions of titanium dioxide (TiO₂ Degussa type P25 was investigated. Under oxygen conditions, irradiation with the Pyrex-filtered out put of 15 W high pressure mercury-arc lamp resulted in complete (more 90 %) mineralization of 50 ppm of TNT, 30 ppm of NB within few hours. At the beginning irradiation, reduction by conduction band electrons may play a more significant role in the photo catalytic degradation of the studied mixtures. The resulted in aromatic ammine compounds were more easily to be oxidized by the hydroxyl radicals.

Keywords: Nitrobenzene, 2,4,6-Trinitrobenzene, UV ray, TiO₂, Photo catalysis.

Introduction

Residues of industrial explosives like 2,4,6 trinitrotoluene (TNT) are a widespread environmental contaminants and have been identified in soil, wastewater and groundwater. TNT is a main nitryl compound in ammunition wastewater. Since World War I, TNT has been used as a major explosive in military ordnance. The extensive research has been conducted for finding effective remediation strategies of these compounds from soil and water environment. The nitro aromatic compounds from water may be treated by physical (adsorption), chemical (oxido reaction), electrochemical and photo oxidative methods.

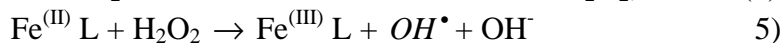
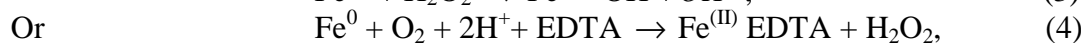
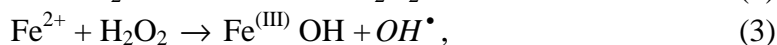
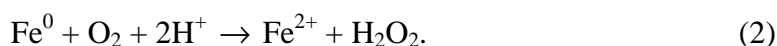
There are many papers focused on using zero-valent iron for removal of the nitro aromatic compounds from water. The Fe⁰-H₂O system in absence of oxygen has been used for reduction

of nitrobenzene, [1]. By this system the aromatic compounds which their nitro nitrobenzene compound is represented was reduced to final aniline produce as follows:



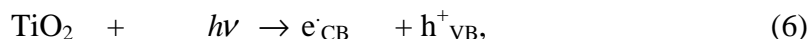
The final amine product may be easily treated by biodegradation methods.

The Fe^0 - H_2O system in presence of oxygen or in presence of both oxygen and a organic ligand like ethylenetetraamine acetic acid (EDTA) exhibits a strong oxidative character so that may oxidize any recalcitrant organic compounds, [2,3] The strong oxidative character of this system has been explained briefly by the following processes:

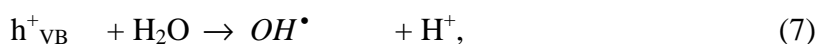


The free radical OH^\bullet appeared in solution played the oxidative role of the system. Due to the free radical OH^\bullet the recalcitrant organic compounds such as nitrobenzene, 2,4,6 trinitrotoluene may be easily mineralized converted into CO_2 , H_2O and other simple inorganic compounds.

The applicability of advanced photochemical oxidation (APO) technologies has been discussed for treatment of contaminated water, air and solids. The authors [4,5,6] have used the photo catalytic technologies for the oxidation of 2,4,6 trinitrotoluene. This article presented data on the photo catalytic degradation of dissolved TNT using aqueous TiO_2 (P25) slurries. This study observed that when a 220 μM solution of TNT was exposed to TiO_2 photo catalyst in the presence of oxygen and near UV radiation more 90% of TNT was oxidized to CO_2 , H_2O and others. The photo degradation and photo catalytic process have promoted oxidation of nitro aromatic compounds. Ultraviolet (UV) oxidation processes generally involve generation of OH^\bullet through UV photolysis of conventional oxidants, including hydrogen peroxide (H_2O_2) and ozone (O_3). The semiconductor (TiO_2) has been preferred for UV oxidation. The TiO_2 photo catalytic mechanism is still being investigated, but its the primary mechanism is believed to proceed as follows, [7,8]:



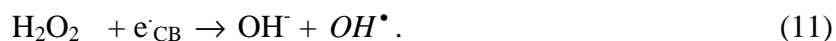
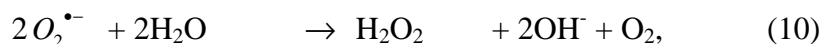
At the TiO_2 surface, the holes react with either H_2O or OH^- from water dissociation to form OH^\bullet as follows:



An additional reaction may occur if the electron in the conduction band reacts with O₂ to form super oxide ions (O₂^{•-}) as follows:



The O₂^{•-} can then react with H₂O to provide additional OH[•], OH⁻ and O₂, as follows:



Thus the TiO₂ photo catalytic technologies have been used for oxidation of nitro aromatic compounds like TNT, phenolic mixtures and others. This article presents a photo degradation of 2,4,6-trinitrotoluene, (TNT) and nitrobenzene, (NB) mixtures in TiO₂ suspension.

Materials and Methods

Chemicals

2,4,6-trinitrobenzene and nitrobenzene were reagent grade from Merck. Titanium dioxide powder (TiO₂), type P25, was obtained from Degussa Corporation. This material, (70% anatase, 30% rutile) has an average particle size of 30 nm and BET surface area of 50 m²g⁻¹. Acetonitrile and other chemicals were used having HPLC reagent grade.

Equipment

A 1L capacity tubular borosilicate glass photo reactor (400mm long, 80mm diameter) was used in all experiments. The reactor walls were covered by aluminum foil and an insulating material to avoid release of radiation and heat to the ambient. The degradation of NB, TNT mixtures was carried out at atmospheric pressure in 0.75 L. of the aqueous solution. During photolysis, the solution was recirculated (300ml/min) by a pump. The studied solutions were prepared with no buffer, so initial pH was governed by addition of an acid or base solutions. Prior to the photo degradation experiments, the suspension of (0.6g/L, TiO₂) with the studied mixtures was stirred for 60 min in the dark to achieve adsorption equilibrium for the organic mixture on the photo catalyst. Oxygen was continuously bubbled with a flow rate of 40L.h⁻¹, into the water bulk (in the reservoir) through a diffuser placed at the side of the reactor.

Continuous photolyses were implemented with a 15-W high pressure mercury – arc lamp, with length of 40 cm, placed at the middle of reactor. The experimental system was established given in Fig. 1.

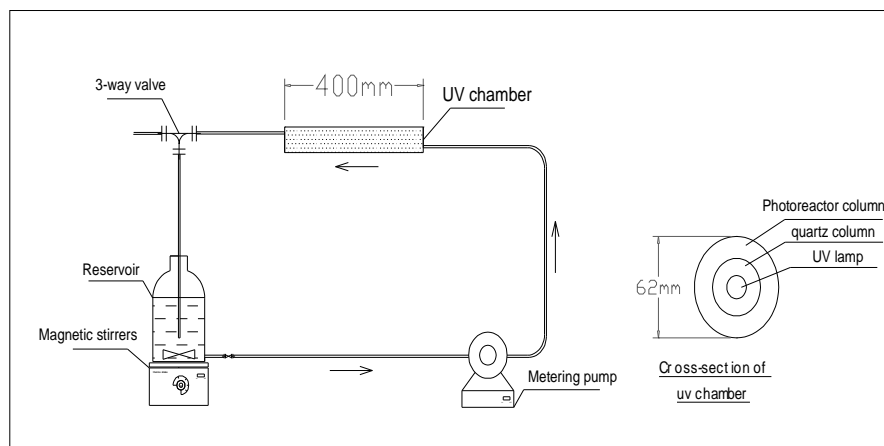


Fig.1. Schematic diagram of the recircular photocatalytic reactor

The excitation wavelengths were confined to the region above 290 nm by use of Pyrex reaction vessels.

Analytical methods

The determination of NB, TNT compounds and its degradation products were carried out on high-performance liquid chromatography (HPLC, Agilent USA) by comparison with the retention time of the standard compounds. Aliquots of 25 μ l were injected into the HPLC to determine concentration of NB compounds and degradation products, running with mobile phase of acetonitrile/water/concentrated H_3PO_4 (v/v/v) at 45/54/0.1. The separation was performed using a Sphesisorb C18 (200 x 4mm) reversed phase column at flow rate of 1.5 ml/min and column temperature of 25⁰C. A Diode array detector was used with the wavelength set at 275 nm. All samples were immediately analyzed to avoid further degradation.

The oxidation of the studied mixture was monitoring by measurement of chemical oxygen demand (COD). COD was analyzed with the potassium dichromate standard procedure and by further titration with iron and ammonium sulphat. Prior to the analysis, the solid (TiO_2) was removed from samples by filtration through MILITEX-HA filter (Millipore, 0.25 μ m).

The relative decrease of COD is calculated by the expression:

$$\text{Relative amount (\%)} = \frac{COD_t}{COD_0} 100.$$

Here COD_0 and COD_t are COD values corresponding to the initial time and to the photo catalyzed t-time.

The conversion or oxidation efficiency of photo catalyzed NB, TNT mixtures is calculated by the expression:

$$\text{Oxidation efficiency (\%)} = \frac{COD_0 - COD_t}{COD_0} 100.$$

Results and Discussion

TiO₂ – catalyzed photolysis of the studied NB,TNT mixtures

At the different initial concentrations of NB,TNT mixtures and in the presence of oxygen or no, the mineralization rates of the mixture evaluated by the decrease of relative COD amounts are changed, Fig.2.

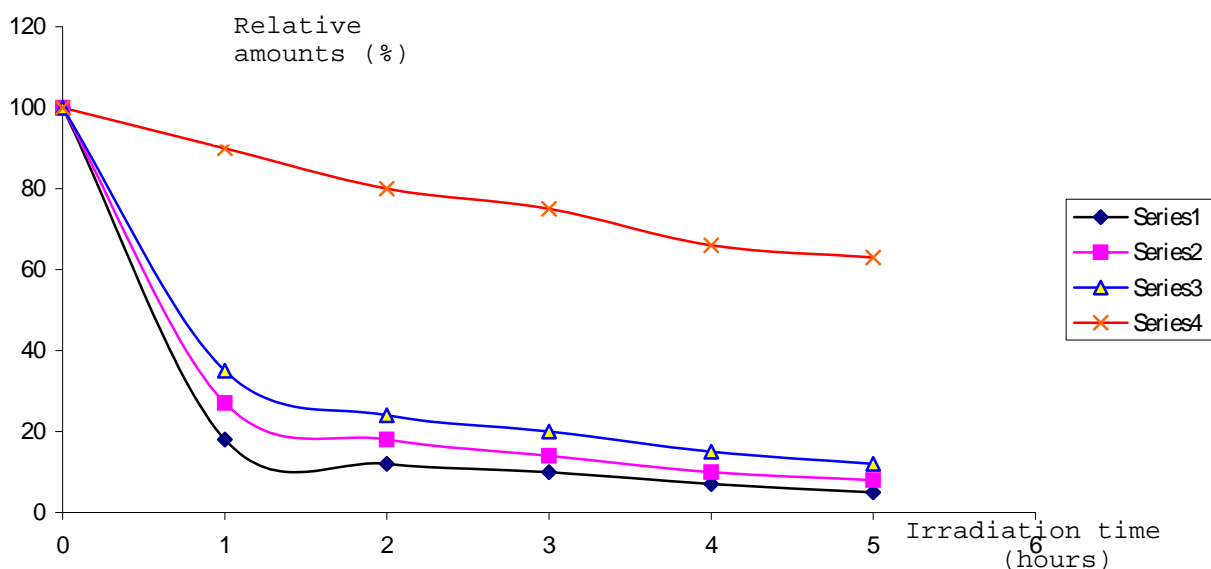


Fig 2. The Time of photodecomposition of the studied mixture with 0.6g/L (TiO₂)

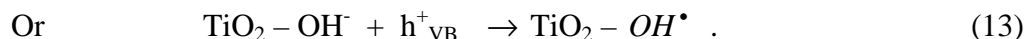
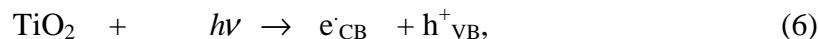
- Series 1: Mixture of TNT (50 ppm), NB (30ppm), in the presence of oxygen.
- Series 2: Mixture of TNT (65 ppm), NB (45ppm), in the presence of oxygen.
- Series 3: Mixture of TNT (75 ppm), NB (55ppm), in the presence of oxygen.
- Series 4: Mixture of TNT (50 ppm), NB (30ppm), without the oxygen.

Fig 2. shows the relative amounts of NB and TNT in the mixture decrease versus the irradiation time on the samples.

When absence of oxygen, the oxidation rates of mixtures were slower than those of the presence of oxygen. When the initial concentrations of the NB, TNT mixtures increased, in the presence of oxygen, the rate of degradation reaction of the mixtures decreased. This is an effect of initial mixture concentration on the kinetics of photo oxidation. As observed from Fig.2, when the initial concentration of NB,TNT mixtures is increased, the corresponding oxidation (mineralization) at any time decreases. The decrease of the degradation rate of the mixtures may be explained by the adsorption of the organic compounds onto the active sites in the TiO₂ particle surface that inhibit the oxidation. These results are similar in the study shown in [9].

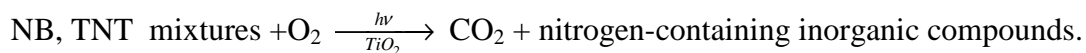
For more two hours photolysed, the oxidation rate of the studied mixtures was slower. This observation may be explained by the formation of the recalcitrant intermediates destroyed hardly.

The TiO₂ photo catalytic degradation of the NB, TNT mixtures is still studied. In our case the photo catalytic oxidation may be suggested as follows:



The considerable evidence supports the assignment of hydroxyl radical, either bound to the semiconductor surface or diffusing freely in solution, as the active oxidizing species in the TiO₂-catalyzed photo oxidation of organic substances.

The simple conversion reaction of the studied mixture may be presented as follows:



Effect of initial pH

The pH of the solution is one of the most important parameters in the photocatalytic reactions because it may affect the surface charge properties of the semiconductor, substrate structure and the equilibrium adsorption. The point of zero charge of Depussa P25 taken from literature has a value of 6.8. Positive surface charge is expected as the solution pH value is lower than the isoelectric point of TiO₂ and negative surface charge is obtained at higher solution values. Fig. 3 shows the results obtained indicating that the effect of initial pH of the mixture. The experimental pH was implemented in the range from 3 to 9. For this pH range, the maximum conversation efficiency (more than 85%) of the studied mixture was achieved at pH values form 7 to 8. This results may be explained by the adsorption of OH⁻ on the TiO₂ surface that enhancing the rate of reaction of photo catalytic degradation.

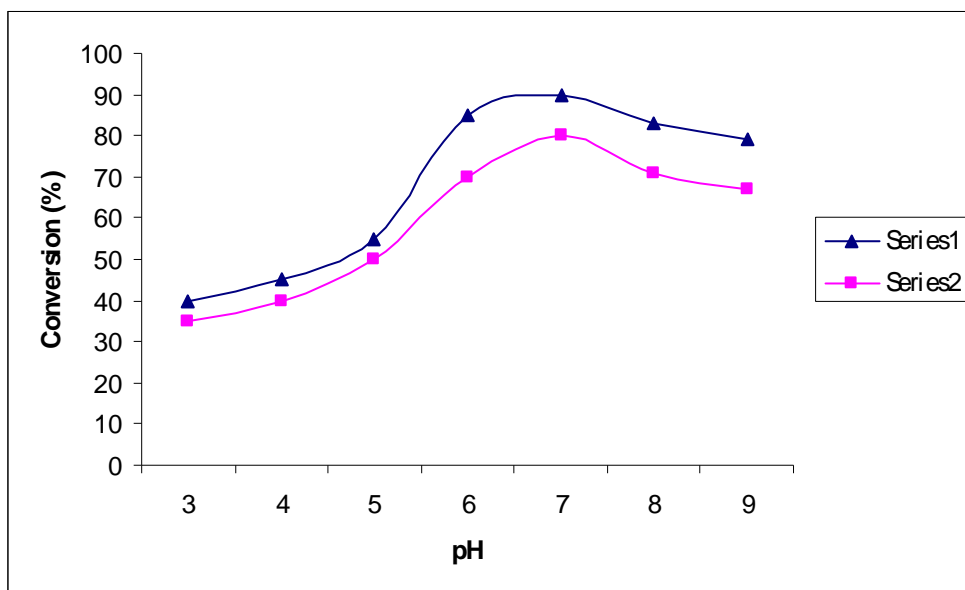


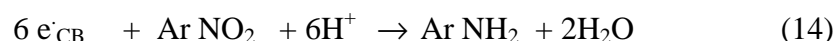
Fig. 3. The dependence of the conversion efficiency of NB, TNT mixtures with TiO_2 , 0.6 g/L, photo catalyzed time 3 hours, on pH,

Series 1. : Mixture of TNT (50ppm), NB (30 ppm), in the presence of oxygen.

Series 2: Mixture of TNT (65ppm), NB (45 ppm), in the presence of oxygen.

The role reduction in the photo catalytic degradation of NB, TNT mixtures

For than one hour photo catalyzed mixture, by normal chemical reaction, we have detected the presence of NH_4^+ ions in solution. The appearance of the NH_4^+ ions in solution indicated that NO_2 groups were reduced during photo catalytic oxidation of the mixtures. The formation of a substantial amount of ammonia in this solution is of interest because it suggests that the degradation pathway involved significant reductive transformation. This evidence has been also discovered in the paper [4]. In practice, the reaction pathway proposing both reductive transformation by conduction band electrons and oxidation by hydroxyl radicals have been reported in the papers [5]. In our case, due to the steric effects and the deactivating influence of the nitro functional groups, the NB, TNT molecules are more highly susceptible to reductive attack than to oxidative one. The experimental data (Fig.4) show the reduction of the nitro groups by conduction band electrons has began earlier than the oxidation of aromatic ring by hydroxyl radicals. For the photo catalyzed time from beginning to 0.6 hours, the conversion rate of NG, TNT mixtures to CO_2 and nitrogen-containing inorganic compounds very low, while in solution NH_4^+ ions have been identified by a normal chemical reaction (Nesle). It is the result of the reduction reaction between conduction band electrons and nitro groups to form an ammine and ammonia respectively:



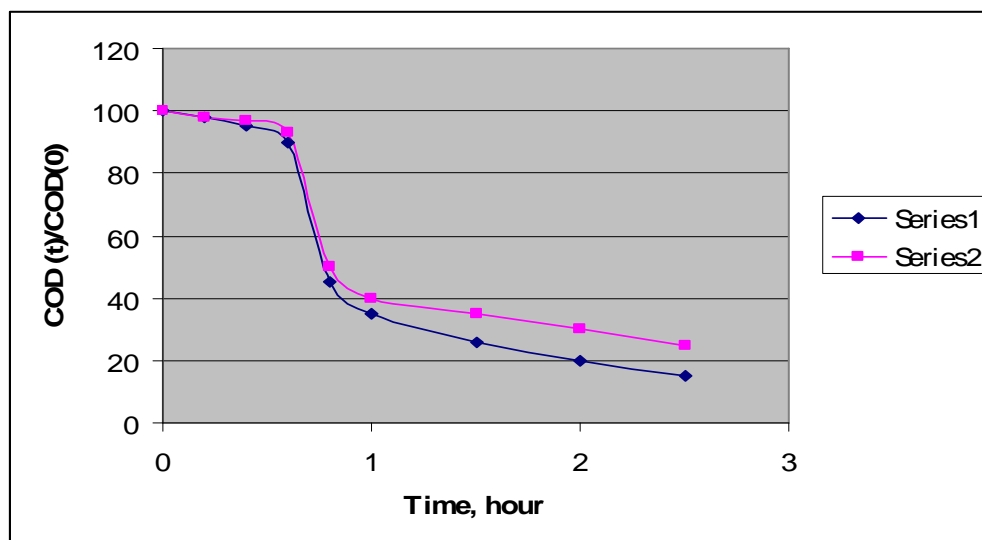


Fig.4. The conversion rate of NB, TNT mixtures versus time photo catalyzed, solution containing 0.2 gTiO₂, pH 6.0 with different concentrations of NB and TNT.

Series 1: Mixture of TNT (50ppm), NB (30 ppm), in the presence of oxygen.

Series 2: Mixture of TNT (65ppm), NB (45 ppm), in the presence of oxygen.

For the photo catalyzed time more than 0.6 hours, the conversion rate of NB, TNT mixtures has become faster. It is maybe the result of the oxidative reaction between hydroxyl radicals and aromatic amines. As known the aromatic amines are more highly susceptible to oxidative attack than parent compounds. This is an interesting thing, that in the studied mixture, between NB and TNT which compound is in favor in reductive process. This problem has been studied in the paper [5]. According to these authors, the reduction by conduction band electrons may play a more significant role in the photo catalytic degradation of TNT than is the case with less substituted nitro aromatic compounds (for example NB).

Conclusion

Direct phot catalytic degradation of NB, TNT mixtures in the presence of oxygen and without oxygen has been studied. In the contrast, complete 90% mineralization of NB, TNT mixtures occurs in an irradiated aqueous slurry of TiO₂ under aerobic conditions. While the detailed mechanism of TiO₂- catalyzed photmineralization has yet to be given, a pathway involving conduction band electrons and hydroxyl radicals as the active reducing and oxidizing species to be discussed. At the beginning time of the radiated mixtures, the reduction of nitro aromatic compounds to form ammine compounds was happen, then it is the oxidation reaction between hydroxyl radicals and aromatic ring.

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