Asian Journal of Chemistry Vol. 22, No. 4 (2010), 3115-3121

Photodegradation of 2,4,6-Trinitrotoluene and Nitrobenzene Mixtures in TiO_2 Suspensions and Their Use for Treatment of Wastewater

NGUYEN VAN CHAT†, DO NGOC KHUE†, NGUYEN VAN HUNG,
TRAN VAN CHUNG* and I. FRANCIS CHENG‡
Department of Analysis, Institute of Chemistry and Material, Hanoi, Vietnam
E-mail: b10p19@vnn.vn

The photo catalytic oxidation of nitrobenzene and 2,4,6-trinitrotoluene mixture in aqueous suspensions of titanium dioxide (TiO_2 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 2,4,6-trinitrotoluene, 30 ppm of nitrobenzene 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 amine compounds were more easily to be oxidized by the hydroxyl radicals.

Key Words: Nitrobenzene, 2,4,6-Trinitrobenzene, UV-Ray, TiO_2, Photo catalysis.

INTRODUCTION

Residues of industrial explosives like 2,4,6-trinitrotoluene (TNT) and nitrobenzene (NB) are a widespread environmental contaminants and have been identified in soil, wastewater and groundwater. 2,4,6-Trinitrotoluene 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 (oxide 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 Fe^0-H_2O system in absence of oxygen has been used for reduction of nitrobenzene[1]. By this system the aromatic compounds such as nitrobenzene was reduced to final aniline product as follows:

$$C_6H_5NO_2 + 3Fe^0 + 6H^+ \rightarrow C_6H_5NH_2 + 3Fe^{2+} + 2H_2O \qquad (1)$$

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 oxygen and an organic

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†Union for Science-Technology of New Products, Hanoi, Vietnam.
‡Department of Chemistry, University of Idaho, Moscow, ID 83844, USA.

ligand like ethylenetretraamine 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:

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \quad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+}OH + OH^{\bullet} + OH^- \quad (3)$$

or,

$$Fe^0 + O_2 + 2H^+ + EDTA \rightarrow Fe^{2+}EDTA + H_2O_2 \quad (4)$$

$$Fe^{2+}L + H_2O_2 \rightarrow Fe^{3+}L + OH^{\bullet} \quad (5)$$

The free radical $OH^{\bullet}$ appeared in solution played role of the oxidation 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 and converted into CO_2, H_2O and other simple inorganic compounds.

The applicability of advanced photo chemical oxidation (APO) technologies has been discussed for treatment of contaminated water, air and soils. The authors[4-6] have used the photo catalytic technologies for the oxidation of TNT from water. This studies presented the data on the photo catalytic degradation of TNT using aqueous TiO_2 (P25) slurries. The study has indicated 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 and H_2O. The photo degradation and photo catalytic process have promoted oxidation of nitro aromatic compounds. Ultraviolet (UV) oxidation processes generally involve generation of UV photolysis of conventional oxidants, including hydrogen peroxide and ozone. The semiconductor (TiO_2) has been preferred for UV oxidation. The TiO_2 photo catalytic mechanism is still being investigated, but the primary mechanism is believed to proceed as follows[7,8]:

$$TiO_2 + h\nu \rightarrow e^{\bullet}_{CB} + h^{+}_{VB} \quad (6)$$

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

$$h^{+}_{VB} + H_2O \rightarrow OH^{\bullet} + H^+ \quad (7)$$

$$h^{+}_{VB} + OH^- \rightarrow OH^{\bullet} \quad (8)$$

An additional reaction may occur if the electron in the conduction band reacts with O_2 to form super oxide ions ($O_2^{\bullet-}$) as follows:

$$e^{\bullet}_{CB} + O_2 \rightarrow O_2^{\bullet-} \quad (9)$$

The $O_2^{\bullet-}$ can then react with H_2O to provide additional $OH^{\bullet}$, OH^- and O_2, as follows:

$$2O_2^{\bullet-} + 2H_2O \rightarrow H_2O_2 + 2OH^- + O_2 \quad (10)$$

$$H_2O_2 + e^{\bullet}_{CB} \rightarrow OH^- + OH^{\bullet} \quad (11)$$

Thus the TiO_2 photo catalytic technologies have been used for oxidation of nitro aromatic compounds like TNT, phenolic mixtures and others.

In this article we present a photocatalytic degradation of TNT and NB mixtures in TiO_2 suspensions.

EXPERIMENTAL

2,4,6-Trinitrobenzene and nitrobenzene were reagent grade from Merck. Titaniun dioxide powder (TiO_2), 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 m^2g^{-1}. Acetonitrile and other chemicals were used having HPLC reagent grade.

Equipment: A capacity tubular borosilicate glass photo reactor (400 mm long, 80 mm diameter) was used in all experiments. The reactor walls were covered by aluminum foil and an insulating material to avoid release of radiation and head to the ambient. The degradation of NB and TNT mixtures was carried out at atmospheric pressure in 0.75 L of the aqueous solution. During photolysis, the solution was recirculated (300 mL/min) by a pump. The studied solutions were prepared without buffer, so initial pH was maintained by addition of an acid or base solutions. Prior to the photo degradation experiments, the suspension of (0.6 g/L, TiO_2) with the studied mixtures was stirred for 1 h in the dark to achieve adsorption equilibrium for the organic mixture on the photo catalyst. Oxygen was continuously bubbled with a flow rate of 40 L h^{-1}, into the water bulk (in the reservoir) throughout 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.

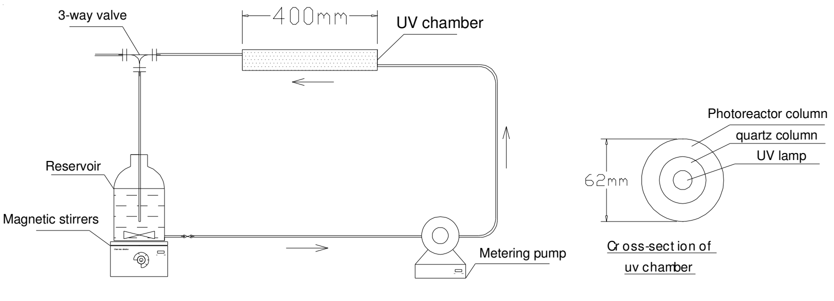

Fig. 1. Schematic diagram of the reclcular phtocatalytic reactor

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

Analytical methods: The determination of degradation products of the mixutre of 2,4,6-trinitrotoluene and nitrobenzene were carried out on high-performance liquid chromatography (Aligent, USA) by comparison with the retention time of the standard compounds. Aliquots of 25 μL were injected into the HPLC to determine concentration of nitrobenzene 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 C_{18} (200 mm × 4 mm) reversed phase column at flow rate of 1.5 mL/min and column temperature of 25 ºC. 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 also monitored by measurement of chemical oxygen demand (COD). The COD was analyzed with the potassium dichromate standard procedure and by further titration with iron and ammonium sulphate. Prior to the analysis, the solid (TiO_2) was removed from samples by filtration through Militex-HA filter (Millipore, 0.25 µm).

The relative decrease of COD is calculated by the expression:

$$\text{Relative amount}\,(\%) = \frac{\text{COD}_t}{\text{COD}_0} \times 100$$

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 photocatalyzed NB and TNT mixtures is calculated by the expression:

$$\text{Oxidation efficiency}\,(\%) = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100$$

RESULTS AND DISCUSSION

TiO_2-catalyzed photolysis of NB and TNT mixtures: At the different initial concentrations of NB and TNT mixtures and in the presence of the oxygen or without oxygen, the mineralization rates of the mixtures evaluated by the decrease of relative COD amounts (Fig. 2). It shows the relative decrease of NB and TNT in the mixtures *versus* the irradiation time. In absence of the oxygen, the oxidation rates of mixtures were slower than those of the presence of the oxygen.

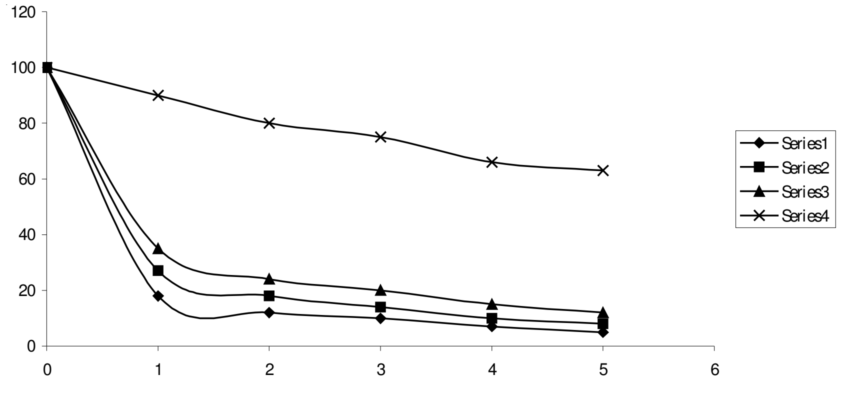

Fig. 2. Time of photodecomposition of the studied mixtures with 0.6 g/L (TiO_2): Series 1: Mixture of TNT (50 ppm), NB (30 ppm), in the presence of oxygen. Series 2: Mixture of TNT (65 ppm), NB (45 ppm), in the presence of oxygen. Series 3: Mixture of TNT (75 ppm), NB (55 ppm), in the presence of oxygen. Series 4: Mixture of TNT (50 ppm), NB (30 ppm), without oxygen.

As observed from Fig. 2, when the initial concentration of NB and TNT mixtures is increased, the corresponding oxidation (mineralization) of the mixtures at any time decreases. This is an effect of initial mixture concentration on the kinetics of photo oxidation. 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 TiO_2 particle surface that inhibit the oxidation. These results are similar to the reported study[9].

After 2 h photolyzed, the oxidation rate of the studied mixtures was slower. This observation may be explained by the formation of the recalcitrant intermediates destroyed hardly.

The TiO_2 photo catalytic degradation mechanism of the NB and TNT mixtures is still not clear. In present case the photocatalytic oxidation process may be suggested as follows:

$$TiO_2 + h\nu \rightarrow e^{\bullet}_{CB} + h^{+}_{VB} \qquad (6)$$

$$\text{or} \quad TiO_2 - H_2O + h^{+}_{VB} \rightarrow TiO_2 - OH^{\bullet} + H^{+} \qquad (12)$$

$$\text{or} \quad TiO_2 - OH^{-} + h^{+}_{VB} \rightarrow TiO_2 - OH^{\bullet} \qquad (13)$$

$$\text{and} \quad O_2 + e^{\bullet}_{CB} \rightarrow O_2^{\bullet-} \qquad (9)$$

$$2O_2^{\bullet-} + 2H_2O \rightarrow H_2O_2 + 2OH^{-} + O_2 \qquad (10)$$

$$H_2O_2 + e^{\bullet}_{CB} \rightarrow OH^{-} + OH^{\bullet} \qquad (11)$$

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 TiO_2-catalyzed photo oxidation of organic substances.

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

$$\text{NB and TNT mixtures} + O_2 \xrightarrow[TiO_2]{h\nu} CO_2 + \text{nitrogen-containing inorganic compounds.}$$

Effect of initial pH: The pH of the solution is one of the most important parameters in the photo calytic reactions because it may affect the surface charge properties of the semiconductor, substrate structure and the equilibrium adsorption. The point of zero charge of Degussa 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 TiO_2 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 3-9. For this pH range, the maximum conversion efficiency (more than 85 %) of the studied mixtures was achieved at pH values form 7-8, for 2 h. This results may be explained by the adsorption of OH^- on the TiO_2 surface that enhance the rate of reaction of photo catalytic degradation.

Role reduction in the photo catalytic degradation of NB and TNT mixtures: After 1 h photo catalyzed mixture, by normal chemical reaction, the presence of NH_4^+ ions is detected in solution. The appearance of the NH_4^+ ions in solution has indicated that NO_2 groups ware 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 also been discovered by Wang and Kutal[4]. In practice, the reaction pathway proposing both reductive transformation by conduction band electrons and oxidation by hydroxyl radicals have been reported by Daniel *et al.*[5]. In present case, due to the steric effects and the deactivating influence of the nitro functional groups, at beginning, the NB and 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 h, the conversion rate of nitrobenzene and 2,4,6-trinitrotoluene mixtures to CO_2. H_2O and nitrogen-containing inorganic compounds very slow, while by a normal chemical reaction in solution NH_4^+ ions have been identified. This is the result of the reduction reaction between conduction band electrons and nitro groups to form an amine and ammonia, respectively:

$$6e^{\bullet}_{CB} + ArNO_2 + 6H^+ \rightarrow ArNH_2 + 2H_2O \qquad (14)$$

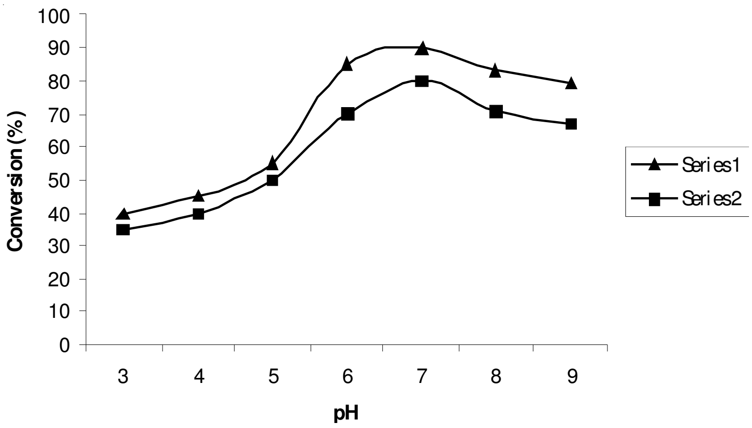

Fig. 3. Dependence of the conversion efficiency of NB and TNT mixture with TiO_2, 0.6 g/L, photo catalyzed time 2 h, on pH, Series 1.: Mixture of TNT (50 ppm), NB (30 ppm), in the presence of oxygen. Series 2: Mixture of TNT (65 ppm), NB (45 ppm), in the presence of oxygen

After the photo catalyzed time more than 0.6 h, the conversion rate of NB and TNT mixtures has become faster. It may be 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. There is an interesting thing, that in the studied mixtures, between NB and TNT which compound is in favor in reductive process. This problem has been studied by Daniel *et al.*[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 (*e.g.* nitrobenzene).

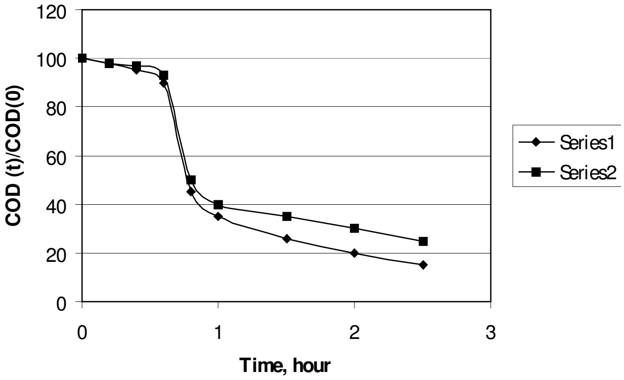

Fig. 4. Conversion rate of NB and TNT mixture *versus* time photo catalyzed, solution containing 0.6 g TiO_2, pH 6.0 with different concentrations of NB and TNT in mixtures. Series 1: Mixture of TNT (50 ppm) and NB (30 ppm), in the presence of oxygen. Series 2: Mixture of TNT (65 ppm) and NB (45 ppm), in the presence of oxygen

Conclusion

Direct photo catalytic degradation of NB and TNT mixtures in the presence of the oxygen and without oxygen has been studied. 90 % Mineralization of NB and TNT mixtures occurs in an irradiated aqueous slurry of TiO_2 under aerobic conditions. While the detailed mechanism of TiO_2-catalyzed photmineralyzation 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 aromatic nitro compounds by conduction band electrons form amine compounds, following is the oxidation reaction between hydroxyl radicals and aromatic ring.

ACKNOWLEDGEMENT

The authors are thankful for the financial support from National Foundation for Science and Technology Development (NAFOSTED).

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(*Received*: 29 July 2009; *Accepted*: 1 January 2010) AJC-8247