CHAPTER-7
CONCLUSIONS

Aromatic nitro compounds are commonly used in a number of industrial processes (manufacture of pesticides, dyes and explosives) and as a consequence they appear as contaminants in many industrial waste waters which finally find a place in surface or ground waters. These substances exhibit potential toxicity, causing serious health problems. Therefore it is highly essential to degrade these toxic chemicals from industrial wastewaters prior to their final disposal. The search for a solution to this problem has involved extensive examinations in the field of wastewater treatment technologies.

In biological methods of treatment activated sludge processing has traditionally been the usual approach for the treatment of municipal sewage and wastewater from many industrial activities. However, it is not feasible to degrade toxic or recalcitrant substances by activated sludge process, since these toxic wastes reduce the biodegradation performance and eventually could inhibit the degradation process (Beltran et al., 2000a).

In physico-chemical methods of treatment, advanced oxidation technologies have been shown to effectively oxidize recalcitrant compounds in wastewater to more readily biodegradable oxidation products that can be treated using a conventional aerobic biological treatment (Sontheimer et al., 1978; Marco et al., 1997; Ledakowicz and Gonera, 1999). In this sense, the interest in the development of sequential chemical and biological processes for the treatment of wastewater has considerably grown (Scott and Ollis, 1995,1997).

Advanced oxidation processes (AOPs), such as heterogeneous photo catalysis have been considered as the most attractive alternative for remediation of toxic organic compounds in wastewater. For the photo catalytic process, the most suitable semiconductor is TiO₂. It is characterized by chemical inertness, non-photo corrosivity, and non-toxic influence on microorganisms. These properties, coupled with its ability to create highly reactive oxidant (hydroxyl radical) on excitation with UV radiation make titanium compounds highly suitable for application in wastewater.
treatment. The hydroxyl radical (·OH) which is known to be one of the most powerful oxidizing species, mineralizes organic pollutants to carbon dioxide and inorganic ions.

Extensive literature is available on application of photocatalysis for the treatment of recalcitrant organic compounds. But very little information is available on photocatalytic degradation of nitro substituted aromatic compounds.

Keeping all these in view the heterogeneous photocatalysis was systematically studied by the author for detoxification and remediation of waste waters contaminated with hazardous chemicals like 2,4-DNP, 2,6-DNP, 2,6-DNT and 1,3-DNB, which are used in manufacture of dye, dye intermediates and in explosives.

The entire work covers the following aspects.

1. Studies on the application of photocatalytic treatment for the degradation and complete mineralization as a pretreatment step to enhance the biodegradability of 2,4-DNP, 2,6-DNP, 2,6-DNT and 1,3-DNB compounds using TiO₂ P-25 (Degussa) as catalyst.

From laboratory scale batch studies the following critical parameters for photocatalytic degradation are examined.

(a) Effect of Catalyst loading
(b) Effect of initial concentration of the compound
(c) Effect of pH
(d) Effect of irradiation time and also
(e) Effect of bubbling of oxygen, nitrogen and air
(f) Effect of nature of the catalysts
(g) Effect of salts like sodium chloride, sodium sulphate and sodium carbonate.

2. Studies on the Biodegradation of the dinitroaromatic compounds with and without photocatalysis to examine the significance of photocatalysis as a pretreatment process.
The following conclusions are drawn from the above studies.

1. Advanced Oxidation Processes based on photocatalysis can be used as a efficient tool for direct detoxification and remediation of the dinitroaromatic compounds. Further they can also be used to enhance their biodegradability in aqueous solutions.

2. The physico-chemical characterization studies of the photo catalysts were carried out to assess the phase purity, surface area, and band gap energy and particle size of the catalysts. These physical properties are essential criterion in the selection of catalysts for photo mineralization studies. The photo catalysts with large band gap and multi phases exhibit greater efficiency. Among the catalysts studied, TiO$_2$ (Degussa P25) was found to be an effective one.

3. In batch recirculation and in batch mode studies 2,4-DNP, 2,6-DNP and 2,6-DNT, 1,3-DNB were successfully degraded in aerated aqueous titanium dioxide Suspensions in the presence of UV light.

4. Efficiency in Photo catalytic degradation increased with an increase in catalyst dosage and reaches an optimum value. At concentrations greater than the optimum, the efficiency began to decrease. The optimal catalyst dosage was found to be 0.3g/250ml for 2,4-DNP, 1g/250ml for 2,6-DNP, 5g/500ml for 2,6-DNT and 3g/800 ml for 1,3-DNB.

5. Efficiency in photo degradation decreased as the initial concentration increases. The optimum concentration for all the four nitro aromatic compounds found were $1.08 \times 10^{-3}$ M in the case of 2,4-DNP & 2,6-DNP. $0.22 \times 10^{-3}$ M for 2,6-DNT, for 1,3-DNB $0.6 \times 10^{-3}$ M with optimum catalyst doses.

6. pH plays a major role in adsorption of pollutants on TiO$_2$ surface. The optimum pH found was pH –8 for 2,4-DNP, 2,6-DNP & 2,6-DNT. Solution natural pH of 6.6 is proved to be the optimum in the case of 1,3-DNB with optimum catalyst doses and with optimum concentrations.
7. The photo catalytic degradation of 2,4-DNP, 2,6-DNP, 2,6-DNT, and 1,3-DNB in TiO$_2$ suspension was found to gradually increase with increasing irradiation period at optimum catalyst loadings and with optimum concentrations. With 4h and 3h of irradiation period the efficiency in photo degradation was about 99% and 100% for 2,4-DNP and 2,6-DNP. With 8 hours of irradiation it was about 73% percent for 2,6-DNT. With 10h of irradiation it was about 95 percent for 1,3-DNB.

Other operational parameters have also been carefully studied and their influences on the photo catalytic degradation have been investigated for the four-nitro aromatic compounds in TiO$_2$ (Degussa) suspensions.

8. In general bubbling of oxygen, nitrogen and air were found to increase the efficiency of the photo catalytic degradation of the studied four di nitroaromatic compounds. Considerable enhancement of degradation was observed for 2,4-DNP and 2,6-DNP with all the three gases and follows the order of oxygen > air > nitrogen while in the case of 2,6-DNT with all the gases the efficiency found to be equal. However in the case of 1,3-DNB the enhancement of the degradation efficiency is less with bubbling nitrogen and the efficiency follows in the order of oxygen > air > nitrogen.

9. The comparative study of different commercial photo catalysts. TiO$_2$ (Degussa), TiO$_2$ (Merek), ZnO, WO$_3$, CdS for the degradation of nitroaromatic compounds under identical experimental conditions revealed that TiO$_2$ (Degussa P-25) was found to have the maximum degradation efficiency. The maximum efficiency may be attributed to the overlap of multi phases of anatase, rutile and amorphous forms in addition to the large band gap. Hence it is concluded that Degussa grade titania particles may be suitable catalyst in the photo mineralization of nitroaromatic compounds.

10. Effect of anions was studied which revealed that photo degradation efficiency gradually decreases with increasing the amount of chloride, carbonate and sulphate ions. They decrease the adsorption of the substrate and also oxygen by competing with two different types of sites, which are considered to exist on the catalyst surface.
The effect of anions on photo catalytic degradation is not much in the case of 2,4- and 2,6- dinitro phenol. The effect is more in the case of 2,6 -dinitro toluene and 1,3- dinitro benzene.

11. In the photo catalytic degradation of these dinitroaromatic compounds it is likely that several polyhydoxylated aromatic intermediates are formed which are due to the substitution of nitro group and hydrogen by OH radical. In the mineralization process, the degradation of nitrogen containing aromatic compounds generates CO$_2$, NO$_2^-$, NO$_3^-$, NH$_4^+$, N$_2$O and N$_2$. NO$_3^-$ is a major and NH$_4^+$ is a minor one. And the large part of CO$_2$ generated may be due to degradation of formic and acetic acids intermediates.

12. The relationship between the reaction rate and the initial concentration of 2,4-DNP, 2,6-DNP, 2,6-DNT and 1,3-DNB was fitted reasonably well to the Langmuir-Hinshelwood kinetic model. Values of the kinetic parameters were calculated from the Langmuir-Hinshelwood equation.

13. Bio kinetic constants were determined using modified Monad modal to study the effect of substrate concentration and the rate of growth in declining growth phase. The kinetic constants $K_s$ (affinity of the organism for the growth-Supporting substrate) and $\mu_m$ (maximum specific growth rate) were derived for pre & post catalysis studies for both mixed cultures and isolated strain. Based on these values it can be concluded that photo catalytic treatment can be also used as a pretreatment step for effective degradation of these recalcitrant compounds. In all the post catalysis experiments isolated cultures showed effective biodegradation in the case of 2,4-DNP, 2,6-DNP & 2,6-DNT while mixed culture exhibited effective degradation in the case of 1,3 DNB.

14. For all the four nitro aromatic compounds the ratio of BOD$_5$/COD, which is normally used to express the biodegradability of the wastewater was 0 before photocatalysis, which improved to 0.4 when photocatalysis was carried as pretreatment. Thus the four-nitro aromatic compounds after the photo catalytic pre treatment can be converted in to biodegradable intermediates, which can be attacked by the microorganisms and mineralized as inorganic ions, carbon dioxide and water.
15. An integrated photo catalytic biological system for the destruction of bio recalcitrant nitroaromatic compounds seems to be a logical choice for the treatment of industrial wastewaters containing nitroaromatic compounds.
CHAPTER 8

SUGGESTIONS AND RECOMMENDATIONS

Advanced Oxidation Processes based on Photocatalysis process has shown to be very effective in the degradation and complete mineralization of toxic dinitro aromatic compounds of 2,4-DNP, 2,6-DNP, 2,6-DNT and 1,3-DNB solutions. The photocatalysis followed by biological degradation also shown to be effective in improving biodegradability of these toxic nitro aromatic compounds. On the basis of present study few suggestions for the continuation of this research are given below.

1. Similar work may be carried out using real industrial wastewaters containing dinitroaromatics and also with solar light instead of Ultra Violet lamps to make the process cost-effective.

2. Different ways can be find out to improve process efficiency by modifying the TiO₂ catalysts (metal semiconductor modification, composite semiconductors and surface sensitization), use of other catalysts and/or adding other extra-electron acceptors.

3. Ultrasonic enhancement of heterogeneous photocatalysis process can be used for enhancing the solubility of less soluble organic compounds to enhance their biodegradability in aqueous solutions.

4. Optimization of conditions for Scaling-up the process has to be studied to gain industrial significance. The high efficiency of the TiO₂ photocatalyst in photocatalytic oxidation is widely known. However, the recovery of the photocatalyst is a major limitation in terms of scale-up possibilities. The investigation of efficient methods of catalyst recovery is a worthwhile study for scale-up implementation.

5. Further investigation may be carried out for integrating photocatalysis and biological waste treatments for complete degradation of hazardous organics.
6. To study kinetic modeling for the combined process for identification of intermediates determination of their toxic or inhibitory properties and their susceptibility to further chemical or biological degradation, which are important in reactor designing. Detailed studies may be performed to identify the microbial degradation pathway(s) in the degradation process of nitroaromatic compounds.
B.Swarnalatha, Ph.D. Thesis

Publications


Communications

B. Swarnalatha and Y. Anjaneyulu (2003) "Photocatalytic Remediation of 1,3-Dinitro Benzene in contaminated water bodies using Aqueous Titanium Dioxide Suspensions" Communicated for 4th International Conference on "Remediation of Chlorinated and Recalcitrant compounds". (Monterey (California), May 24-27, 2004)


B. Swarnalatha, B. Madhavi Prakash, Y. Anjaneyulu "Application of Ultrasonic Cavitation for High Efficiency Degradation of Non-Biodegradable Toxic Organic
B.Swarnalatha, Ph.D. Thesis  