Middle-East Journal of Scientific Research 20 (12): 2506-2510, 2014
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2014.20.12.297

# Application of Photocatalytic Process for Removal of Hydrazoic Acid from Waste Air

*R. Cattallany and S. Ghanbari*

Faculty of Chemical Engineering,
Malek-ashtar University of Technology, Tehran, Iran

**Abstract:** The treatment of hydrazoic acid contaminated in waste air was studied using photocatalytic reactor. The $TiO_2$ photocatalyst was prepared by dissolved $TiO_2$ powder in ethanol and coated on glass tube medium. The $TiO_2$ coated on the media was characterized by Scanning Electron Microscope (SEM). The thin films $TiO_2$ coated media was packed in continuous flow treatment system with UV light irradiation. The hydrazoic acid treatment efficiency in continuous mode of fixed bed column were studied on the number of UV light (1-6 lamps) and waste air flow rate (0.25-1 L/min). The hydrazoic acid concentration of waste air used in the photocatalytic reactor was constantly controlled at 200 ppmv. The results illustrated that all parameters play an important role in the treatment of waste air. The hydrazoic acid removal efficiency of the photocatalytic system was increased with increasing in the $TiO_2$ loading and number of lamp and decreasing flow rates. These results can be applied as guidance in the hydrazoic acid treatment in industrial scale.

**Key words:** Hydrazoic acid · Photocatalytic reactor · $TiO_2$ · UV.

## INTRODUCTION

The industrial production of sodium azide ($NaN_3$) has surged over the past decade to meet the demand for automobile airbag inflator propellant. However it is highly toxic-even a cursory search of the Internet reveals that sodium azide toxicity is comparable to that of sodium cyanide when ingested [1-3]. Air bag is currently a necessary item in new motor vehicles for protection of human life. In a motor vehicle, air bag is designed to give the maximum protection in an accident of the driver and the passenger in the front seat. This safety device was first introduced in the late 1980. Since, then there has been considerable popularity in incorporating this safety device into all new motor vehicles. In the air bag, sodium azide is the key component. Due to increasing demand for this product in recent years, annual production of sodium azide has far exceeded 5 million kg [3-6] and this demand is expected to continue for the foreseeable future.

The smooth, rapid thermal decomposition characteristics, the high specific nitrogen content (65 mol%) and the long shelf life make sodium azide an attractive propellant material [7-9].

$$NaN_3 \rightarrow Na + 3/2N_2 \qquad (1)$$

There are three chemical compounds in an air bag, sodium azide ($NaN_3$), potassium nitrate ($KNO_3$) and silicon dioxide ($SiO_2$). When the motor vehicle is hit or suffers from severe deceleration, a rapid chemical reaction (or mild detonation) is triggered by an electric device and the air bag is inflated in a matter of millisecond [9]. The chemical reactions involved in the gas generation include [5, 10]:

$$2NaN_3 \rightarrow 2Na + 3N_2;\ T > 300C \qquad (2)$$

$$10Na + 2KNO_3 \rightarrow K_2O + 5Na_2O + N_2 \qquad (3)$$

$$K_2O + SiO_2 + 5Na_2O \rightarrow \text{alkaline silicate} \qquad (4)$$

Sodium azide has other uses. In the 1970s, it was used in some registered pesticide formulations, mainly for crops and consequently discarded commercial products, off-specification product, container residues and spill residues were listed as hazardous waste by the United States Environmental Protection Agency (EPA) [11]. Lately, interest in sodium azide pesticide formulation has been revived as a replacement for methyl bromide [12]. Azide can also combine with metals to form explosive metal–azide complexes. The accumulation of azide in laboratory apparatus and drains, where it can react with lead or copper-containing fixtures, has caused explosions when routine maintenance work has been attempted [1].

---

**Corresponding Author:** Ghanbari, Faculty of Chemical Engineering, Malek-ashtar University of Technology, Tehran, Iran. Tel: +982122970233.

The azide ion is readily protonated in aqueous solution (pKa= 4.65) to yield volatile hydrazoic acid ($HN_3$), which is itself toxic, so the atmospheric fate of azide substance is also of interest and has recently been described [1, 3, 13].

Sodium azide is highly soluble, which implies that releases into the environment could potentially migrate into sewers, streams, lakes and groundwater systems. Because of its ready availability and high toxicity, sodium azide has become a chemical of interest for many institutes and departments (Department of Homeland Security EPA Water Supply Security Division) [1]. In the literature, there is relatively very little work done on the disposal of sodium azide in aqueous solution or air environment. Many researchers considered various reaction and kinetic aspects of ozonation of hydrazoic acid in aqueous solution. These investigators had shown that ozonation can effectively convert hydrazoic acid in aqueous solution into various nitrogeneous compounds, including $N_2$, $NO_2^-$, $NO_3^-$ and $NO_x$ [5]. Ozonation is also used for the removal of alkali metal azides from water and wastewater. By oxidation of alkali metal azide by ozone gas, these compounds convert to nitrogen and alkali metal nitrate. However this method (ozonation) is not suitable for the treatment of sodium azide in highly alkaline solutions [5].

The aim of this research was to study the effect of operating parameters on photocatalytic reactor using $TiO_2$ photocatalyst for the treatment of Hydrazoic acid in waste air. The catalyst was coated on cylindrical glass and packed in the continuous down flow fixed bed column system with UV light irradiation. The controlled parameters of Hydrazoic acid treatment system by photocatalytic reactor consisting of number of UV lamps (1-6 lamps) and waste air flow rate (1-10 L/min) were evaluated on Hydrazoic acid treatment efficiency.

## MATERIALS AND METHODS

**Materials:** Titanium dioxide ($TiO_2$) nanocrystallites powder purchased from Danesh Shimi Azma Co. (Tehran, Iran). The stock azide solution was prepared using $NaN_3$ obtained from Danesh Shimi Azma Co. Ethanol (95%; Commercial) was used as solvent. UV lamps (8W, Philips, Netherland) with a wavelength of 200-250 nm were a light source for photocatalytic performing in this work.

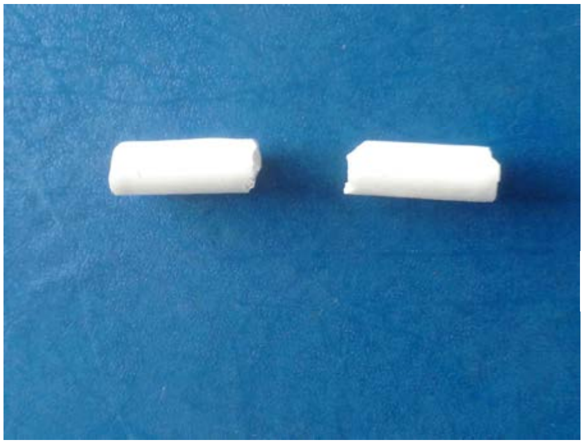

Fig. 1: $TiO_2$ powder on glass tubes catalysts.

**Catalyst Preparation:** Catalyst was prepared by dissolving 6 g of $TiO_2$ powder in 150 ml of ethanol. After vigorously stirring for 2 h at room temperature, polyethylene glycol (PEG) was added to the solutions and served as precursor solutions for binder. Hydrolysis reaction occurred during stirring to achieve $TiO_2$ sol. Glass tubes (6 mm diameter and 1.5 cm height) were used as the medium for $TiO_2$ thin film coating. The $TiO_2$ film was formed on the medium by dip coating method using the precursor solutions at ambient atmosphere. Then it was dried at 100°C for 1 h and calcined at 600°C for 2 h. It performed in air flowing and cooled down at a rate of 10°C/min to complete the step and get $TiO_2$ catalyst media [14]. The $TiO_2$ coated glass tubes were shown in Figure 1.

**Photocatalytic Experimental Set Up:** The photocatalytic system with $TiO_2$ on glass medium was set up by laboratory scale. Continuous down flow fixed-bed glass columns were installed in stainless steel chamber. UV lights of 1 to 6 lamps were vertically fixed inside of the chamber wall. The UV lamps were chosen at 200-250 nm of wavelength (power consumption of 8 W per lamp). The air stream was flowed through the reactor chamber to reduce the system temperature. The diagram of hydrazoic acid contaminated waste air and photocatalytic system are demonstrated in Figure 2. The waste air stream was generated for hydrazoic acid treatment testing by photocatalytic system. Air flow from air compressor was passed through a hydrazoic acid reservoir (20 % w/w) to pick up vaporized gas and moisture at room temperature (20°C). The mixed stream was continuously flowed through the holding tank and steady flow to the photocatalytic reactor.

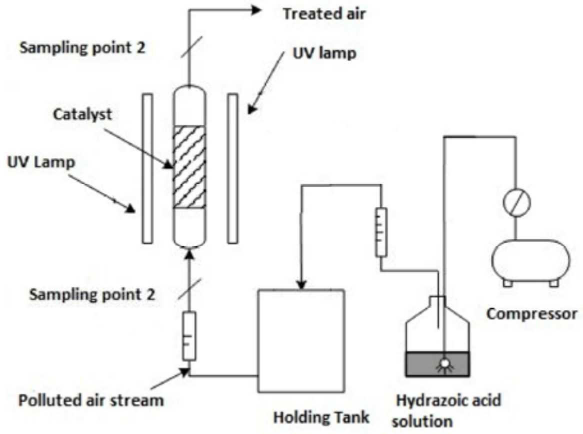

Fig. 2: Schematic diagram of Experimental set up

## RESULTS AND DISCUSSIONS

**Scanning Electron Micrographs of $TiO_2$ Films:** A dip coating method on the small glass tubes described in pervious Section was employed to effectively perform the catalytic preparation with suspension of pure $TiO_2$ nano powder, ethanol solvent and polyethylene glycol as binder. Figure 3 shows the scanning electron microscope of the surface of the synthesized $TiO_2$ on one of the glass tubes. It is observed that $TiO_2$ nanoparticles were well dispersed on the surface of the glass tube substrate. $TiO_2$ surface is rough and large size particles are formed on the surface [6, 14].

**Stability of $TiO_2$ Catalyst on Waste Air Treatment:** $TiO_2$ photocatalyst coated on glass tubes was used for the treatment of polluted air in hydrazoic acid concentration of 200 ppmv. The glass tubes were packed in a raschig-ring typed packing media to increase the contact area among the catalyst, UV light and the waste gas. The efficiency and stability of $TiO_2$ catalyst on acid treatment from the waste air using photocatalytic reactor were investigated by plotting between hydrazoic acid treatment efficiency and irradiation time, as shown in Figure 4. Tests were performed three times under the same testing conditions to verify stability of the synthesized catalyst and the system. Efficiency treatment was monitored for consistency of the system every 10 minutes for 1.5 hours.

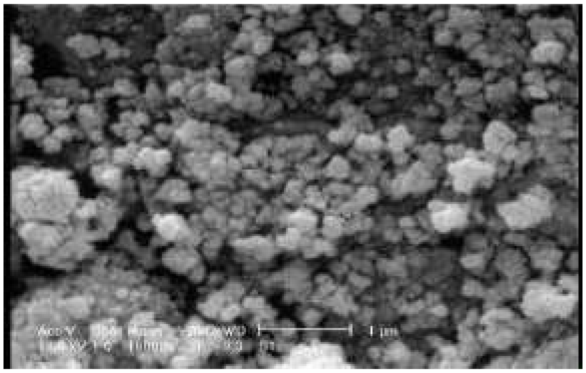

Fig. 3: SEM image of the surface of $TiO_2$ on glass tube substrate of $TiO_2$ suspension.

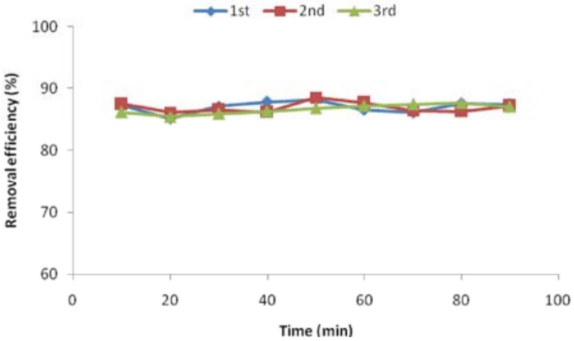

Fig. 4: Waste air treatment efficiency versus irradiation time using continuous $TiO_2$photo-reactor.

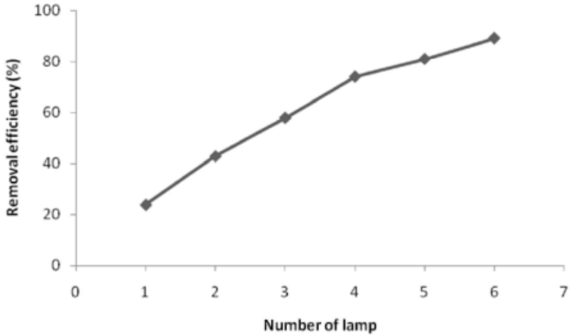

Fig. 5: Effect of UV light irradiation on hydrazoic acid treatment from waste air by continuous photocatalytic reactor.

The results show that $TiO_2$ catalyst on the raschigring typed glass packing media performed effectively in the treatment with constant efficiency throughout the operating time of 1.5 hours. After repeated operations, similar performance of the system with 89.43% efficiency was obtained. This indicates stability of the $TiO_2$ coated catalysts packed in the photoreactor column exposing to waste air flow and UV light irradiation. Also the $TiO_2$ catalyst, under constantly and continuously high activity UV light exposure, can effectively be regenerated after reacting with hydrazoic acid in the waste air.

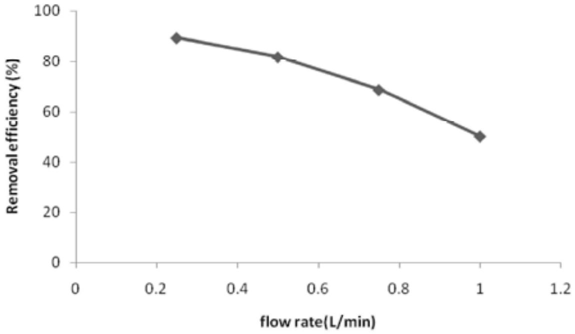

Fig. 6: Effect of waste air flow rate on hydrazoic acid removal efficiency (%) by the $TiO_2$ photocatalytic system.

**Effects of UV Light Irradiation:** The 1-6 UV lights were vertically fixed inside the stainless chamber around the photo-reactor column. The effect of UV light irradiation on photocatalytic performing was studied by varying the number of UV lamps that can implies for intensity of the light source. The UV light intensity was an important parameter for treatment using $TiO_2$ photocatalyst in the photo-reactor. The curve of NH treatment efficiency versus irradiation time was manifested in Figure 5.

The results indicated that the increasing in the irradiation intensity by increasing the number of UV lamps enhanced the treatment efficiency. Light intensity is a major factor in photocatalytic reactions, because electron–hole pairs can be produced by light energy [14, 15]. There were more photons per unit time and unit area at higher light intensity. Thus the chances of photon activation on photocatalyst surface were also increased. Therefore, 6 lamps was the strongest effect to the treatment of hydrazoic acid in waste air. In case of turn off the UV light irradiation the treatment of acid waste air was not occurred with <10% treatment efficiency.

**Effects of Waste Air Flow Rate:** The effect of waste air flow rate on the hydrazoic acid treatment efficiency was studied using 6 lamps of black light lamp. The effect of waste air flow rate on hydrazoic acid treatment efficiency at 200 ppmv of hydrazoic acid concentration was manifested in Figure 6. The result demonstrated that hydrazoic acid treatment efficiency was decreased when waste air flow rate was increased from 0.25 to 1 L/min. At 0.25 L/min waste air flow rate provides the maximum hydrazoic acid treatment efficiency. In consequence of higher waste air flow rate, the contact time between hydrazoic acid in waste air and catalyst surface was reduced [14].

## CONCLUSIONS

The removal of hydrazoic acid in waste air using coated $TiO_2$ photocatalyst in continuous photo-reactor was investigated. The $TiO_2$ photocatalyst was effectively synthesized and s table for the treatment of waste air. The influences of the number of UV ligh and waste air flow rate in hydrazoic acid treatment were measured. The treatment of hydrazoic acid using the photocatalyst was found to be significantly affected by all parameters. The results of this study would be used as a guide for the further design and operation of industrial-scale systems.

## REFERENCES

1. Betterton, E.A., J. Lowry, R. Ingamells and B. Venner, 2010. Kinetics and mechanism of the reaction of sodium azide with hypochlorite in aqueous solution. Journal of Hazardous Materials, 182(1): 716-722.
2. Smith, R.P. and D.E. Wilcox, 1994. Toxicology of selected nitric oxide-donating xenobiotics, with particular reference to azide. CRC Critical Reviews in Toxicology, 24(4): 355-377.
3. Betterton, E.A. and J.L. Robinson, 1997. Henry's law coefficient of hydrazoic acid. Journal of the Air & Waste Management Association, 47(11): 1216-1219.
4. Betterton, E.A. and D. Craig, 1999. Kinetics and mechanism of the reaction of azide with ozone in aqueous solution. Journal of the Air & Waste Management Association, 49(11): 1347-1354.
5. Lin, S.H. and C.P. Huang, 2001. Adsorption of hydrazoic acid from aqueous solution by macroreticular resin. Journal of hazardous materials, 84(2): 217-228.
6. Slamet, H.W.N., E. Purnama, K. Riyani and J. Gunlazuardi, 2009. Effect of copper species in a photocatalytic synthesis of methanol from carbon dioxide over copper-doped titania catalysts. World Applied Sciences Journal, 6(1): 112-122.
7. Hitt, J., 1992. Automobile airbag industry toxic exposures. Hazardous materials toxicology: clinical principles of environmental health. Baltimore, MD: Williams & Wilkins.
8. Betterton, E.A., 2003. Environmental fate of sodium azide derived from automobile airbags. Critical Reviews In Environmental Science And Technology, 33(4): 423-458.
9. Al-Qurainy, F., 2009. Effects of sodium azide on growth and yield traits of Eruca sativa (L.). World Applied Sciences Journal, 7(2): 220-226.

10. Madlung, A., 1996. The chemistry behind the air bag: High tech in first-year chemistry. Journal Of Chemical Education, 73(4): 347.
11. Ketchersid, M. and M. Merkle, 1976. Dissipation and phytotoxicity of sodium azide in soil. Weed Science, pp: 312-315.
12. Santos, B.M., J.P. Gilreath, T.N. Motis, J.W. Noling, J.P. Jones and J.A. Norton, 2006. Comparing methyl bromide alternatives for soilborne disease, nematode and weed management in fresh market tomato. Crop Protection, 25(7): 690-695.
13. Orlando, J.J., G.S. Tyndall, E.A. Betterton, J. Lowry and S.T. Stegall, 2005. Atmospheric chemistry of hydrazoic acid ($HN_3$): UV absorption spectrum, HO reaction rate and reactions of the $N_3$ radical. Environmental Science & Technology, 39(6): 1632-1640.
14. Pongyeela, P., J. Chungsiriporn, P. Kaewpradit and L. Sikong, 2013. Process modeling of $NH_3$ contaminated waste air treatment in photocatalytic reactor using $TiO_2$ coated glass tubes. Songklanakarin J. Sci. Technol., 35(3): 361-368.
15. Li, Y., S. Sun, M. Ma, Y. Ouyang and W. Yan, 2008. Kinetic study and model of the photocatalytic degradation of rhodamine B (RhB) by a $TiO_2$-coated activated carbon catalyst: Effects of initial RhB content, light intensity and $TiO_2$ content in the catalyst. Chemical Engineering Journal, 142(2): 147-155.