Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 3, No. 12, p. 36-42, 2013
http://www.innspub.net

RESEARCH PAPER

# Photo catalytic degradation of acrylonitrile in aqueous solutions using nano titanium Dioxide

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**Key words:** Acrylonitrile, kinetics, nano $TiO_2$, photo catalysis, UV irradiation.

## Abstract

In the present study, photocatalytic decomposition of Acrylonitrile (ACN) using nano titanium dioxide was investigated. The effects of influential parameters such as ACN initial concentration, solution pH, catalyst loading, inorganic salts and the type of light sources on the reaction rate were evaluated, and optimum conditions were determined. The results of experiments showed that catalyst loading of 0.1 g/l $TiO_2$ was the optimum and further increase in the $TiO_2$ loading reduced removal efficiency. The highest photodegradation reaction rate was obtained in slightly alkaline condition rather than neutral or acidic condition. The experimental data showed that the photocatalytic degradation of ACN can be simulated by using pseudo-first-order reaction rate expression. It was concluded that photocatalytic process offers an interesting prospect for its application to the treatment of wastewater streams containing ACN.

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## Introduction

The contamination of groundwater and surface water by volatile organic compounds (VOCs) has become a worldwide environment problem because of the many adverse effects of these pollutants. Acrylonitrile (ACN) is one of the VOCs used in large quantities as an important industrial material for production of acrylamide, acrylic fibers, plastics and synthetic rubbers; consequently, it is present in many industrial effluents. The extensive use of ACN in various industries has led to the widespread introduction of this compound into the environment. The most important physicochemical properties of acrylonitrile are presented in Table 1.

**Table 1.** Some physicochemical properties of acrylonitrile.

| **Properties** | **value** |
|---|---|
| Molecular formula | $C_3H_3N$ |
| Molar mass | 53.06 g/ mol |
| Density | 0.81 g/cm$^3$ |
| Melting point | -84 °C |
| Boiling point | 77 °C |
| Appearance | Colorless liquid |

ACN is the third item in the EPA list of 129 priority pollutants and the current recommendation for this compound in lakes and streams is <0.058 ppb to prevent possible health effects (Zhang and Pierce, 2009; Shakerkhatibi *et al.*, 2010). In spite of the long production history of this compound, difficulties remain in treatment of ACN contaminated wastewater streams (Shin *et al.*, 2009).

Although several VOC control technologies such as adsorption (Kumar *et al.*, 2008), air stripping (Freeman *et al.*, 1984), biological treatment (Wang *et al.*, 2010; Shakerkhatibi *et al.*, 2010), advanced oxidation processes (Chang *et al.*, 1997) and pervaporation process (Aliabadi *et al.*, 2011) have been studied for the removal of ACN from aqueous streams, but development of new technologies for the removal of this compound from dilute streams is necessary.

Photocatalytic oxidation has been proposed as an effective method for treatment of toxic compounds and polluted water (Kabra *et al.*, 2004). Among all newly developed detoxification methods, heterogeneous photocatalytic oxidation is becoming more and more popular each day. One of the photocatalysts which has received a great deal of attention from research circles is titanium dioxide ($TiO_2$). Among the metal oxide and semiconductors suitable for photocatalytic processes, $TiO_2$ in its anatase form is the most broadly used one because, it is highly active, available, and chemically resistant in all reaction conditions and it has high ability to destroy a wide range of contaminants using solar or UV irradiation (Haque *et al.*, 2005). The ultimate product of the photocatalytic process can be $CO_2$ and $H_2O$ and relevant inorganic ions such as nitrate or chloride. However, in certain cases facile mineralization to $CO_2$ does not occur due to the formation of a stable intermediate that is recalcitrant to $TiO_2$ photooxidation (Friesen *et al.*, 1999).

The aim of this research is to study the photocatalytic degradation of ACN in the presence of $TiO_2$. To the best of our knowledge, photocatalytic degradation of ACN in aqueous solutions using nano titanium dioxide has not been reported in the literature. In the present study, the potential of UV/$TiO_2$ process for the treatment of ACN contaminated water was evaluated and the effects of different operational parameters on the removal efficiency were investigated.

## Materials and methods

### *Materials*

ACN (99% purity) was purchased from Fluka. Degussa P25 (80% anatase and 20% rutile, BET specific surface area, SSA: 50 m$^2$g$^{-1}$ and with a mean size of 21nm) was used as photocatalyst. Other chemicals were purchased from Merck (Darmstadt, Germany) with a purity of >99% and deionized laboratory water was used for making aqueous mixtures. Initial pH of the solution was adjusted by using 0.1N NaOH and 0.1N HCL.

### Photoreactor

A cylindrical stainless steel reactor of 1000ml capacity was used as a reaction vessel in which three UV lamps were inserted as light source. The photoreactor lid was provided with ports for the inlet and outlet of gases and sampling. The reactor walls were covered by aluminum foil to avoid release of UV radiation out of the reactor. The $TiO_2$ suspension in aqueous ACN solutions was irradiated in the reactor with three UV lamps. Various UV light sources tested, including UVC lamp (Philips TUV 6W, low pressure Hg lamp close to monochromatic output at 254 nm, Poland) and UVA lamp (Hitachi F6T5 6W, Black Light, 365 nm, Japan). Each lamp was placed in a quartz tube to preventing direct contact with ACN solution, and immersed in the solution.

### Procedure

1000ml of the ACN solution and $TiO_2$ catalyst were transferred into the reactor. This suspension was continuously aerated for 15 min to reach equilibrium in the darkness. The lamps were then switched on to initiate the photoreaction. Agitation and aeration were maintained at a fixed level during the reaction to keep the suspension homogeneous. Samples (5 mL) were taken at regular time intervals then centrifuged, filtered and analyzed by HPLC.

### Analysis

The concentration of ACN in the aqueous solutions was measured by HPLC (Adept, Cecil Instruments, UK) equipped with a reverse-phase C18 Hichrom column (5µm, 4.6×150mm). The mobile phase was 75% acetonitrile and 25% water. ACN concentration was determined using an injection volume of 20 µl at 195 nm wavelengths (UV detector) and a mobile phase flow rate of 1 ml/min.

## Results and Discussion

### Reaction kinetics

Reaction kinetics gives information about the reaction rates and the mechanisms by which the reactants are converted to the products. The experimental results showed that the photocatalytic degradation of ACN obey apparently pseudo-first order kinetics at low initial ACN concentration. The removal rate of ACN is therefore expressed as:

$$-\frac{dC}{dt} = k_{obs}C \qquad (1)$$

Integration of this equation from $C = C_0$ to $C = C$ yield the following equation:

$$-Ln(\frac{C}{C_0}) = k_{obs}t \qquad (2)$$

where $C$ is the concentration of ACN at time *t*, $C_o$ the initial concentration of ACN and $K_{obs}$ the pseudo-first order rate constant.

### Effect of Catalyst Loading

**Table 2.** The pseudo-first order reaction rate constants for the photocatalytic degradation of ACN at various catalysts loading.

| **Catalyst Loading** | **$K_{obs}$** | **$R^2$** |
|---|---|---|
| 0.0 g/l | 0.004 | 0.98 |
| 0.05 g/l | 0.011 | 0.96 |
| 0.1 g/l | 0.014 | 0.98 |
| 0.3 g/l | 0.009 | 0.72 |
| 0.5 g/l | 0.008 | 0.69 |

For economic removal of pollutants from aqueous solutions, it is necessary to find out the optimum catalyst loading for efficient degradation. The effect of catalyst loading on the removal efficiency of ACN was investigated in the range of 0 to 0.5 g/l. The results are presented in Table 2. and Fig. 1.

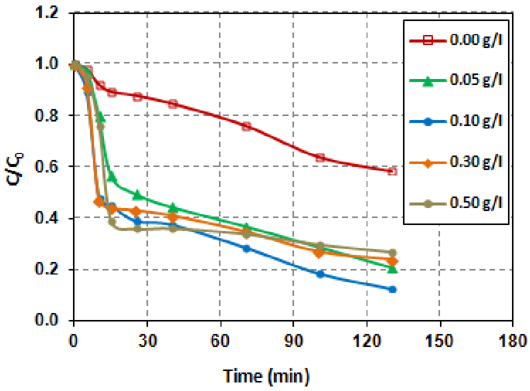

**Fig. 1.** Effect of $TiO_2$ loading on the photo catalytic degradation of CAN.

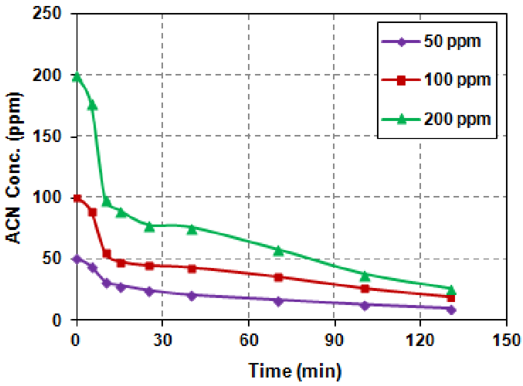

**Fig. 2,** Effect of initial concentration on the photo catalytic degradation of CAN.

As can be seen, ACN was removed more efficiently by increasing the amount of catalyst loading from 0 to 0.1 g/l. This is probably because of higher surface area of $TiO_2$ nano particles which is available for photons and ACN molecules adsorption. By increasing the catalyst loading more than 0.1 g/l, the removal efficiency of ACN decreased. This may be attributed to aggregation of $TiO_2$ particles at excess loading, which causes a decrease in the number of surface active sites and increase in opacity and light scattering by $TiO_2$ particles that decreases the light penetration in the solution that result in a consequent rate decrease (Xu *et al.*, 2009; Sauer *et al.*, 2002).

As stated above, the optimum amount of catalyst loading was found to be 0.1 g/l for the degradation of ACN. Hence, this amount was selected as the optimum value for further experiments.

*Effect of initial ACN concentration*

Successful application of photocatalytic oxidation system requires the investigation of the dependence of photocatalytic degradation rate on the substrate concentration (Aliabadi and Sagharigar, 2011). The effect of initial ACN concentration on the degradation rate of ACN during the reaction time is presented in Fig 2.

The photo catalytic degradation rate of ACN was shown to increase with the increase in initial concentration from 50 to 200 ppm. It has been indicated in several researches that as the concentration of the target pollutant increases, more and more molecules of the compound are adsorbed on the surface of the photocatalyst.

*Effect of inorganic salts*

Several researchers have demonstrated that the presence of inorganic ions may influence the kinetics and mechanism of the transformation processes of organic compounds. Consequently, the basic understanding of the effects of inorganic constituents present in wastewater is crucial to ensure operational stability of the process. Several studies have indicated that the presence of various components such as calcium, magnesium, iron, zinc, copper, bicarbonate, phosphate, nitrate, sulphate, chloride, and dissolved organic matters have substantial influences on the photocatalytic oxidation of organic pollutants since they can be adsorbed onto the surface of $TiO_2$ (Abdullah *et al.*, 1990). In addition, depending on the solution pH, they can also compete with the target pollutant for the active sites.

The effect of inorganic ions (chloride, carbonate, bicarbonate, nitrate and sulfate) on the photocatalytic degradation of ACN during the reaction time is shown in Fig. 3. The effects of the presence of common anions, were studied using the corresponding sodium salts. All the experiments were carried out using 2.5mM solutions of the anions with initial ACN concentration of 200 ppm and catalyst loading of 0.1g/l. The effect of the presence of these anions on photocatalytic degradation rate of ACN showed the following trend:

$CO_3^{2-} < HCO_3^- < SO_4^{2-} < NO_3^- < HCO_3^-$

As can be seen from Fig.3, photocatalytic degradation rate was affected significantly in the presence of bicarbonate and chloride. This is due to the fact that inorganic ions act as hydroxyl radical scavengers and absorb UV light through the following reactions:

$CO_3^{2-} + HO^\bullet \rightarrow HO^- + CO_3^{-\bullet}$ (3)

$HCO_3^{2-} + HO^\bullet \rightarrow CO_3^{-\bullet} + H_2O$ (4)

These ions might also block the active sites of the catalyst surface thus deactivating the catalyst towards the organic molecules.

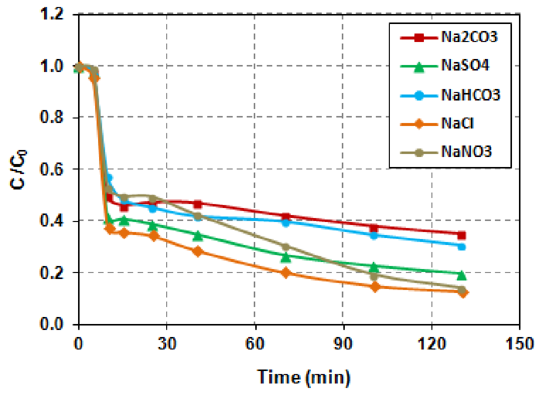

**Fig. 3.** Effect of inorganic salts on the photo catalytic degradation of CAN.

The pseudo-first order reaction rate constants obtained for the photo catalytic degradation of ACN in the presence of various anions are presented in Table 3.

**Table 3.** The pseudo-first order reaction rate constants for the photo catalytic degradation of ACN in the presence of various anions.

| **Anions** | **$K_{obs}$** | **$R^2$** |
|---|---|---|
| carbonate | 0.0028 | 0.95 |
| Sulfate | 0.0066 | 0.99 |
| Bicarbonate | 0.0043 | 0.93 |
| Chloride | 0.0095 | 0.99 |
| Nitrate | 0.0113 | 0.99 |

*Effect of pH*

The effects of initial pH on the photocatalytic process is more complex and generally depends on the type of pollutant and the zero point charge (zpc) of photocatalyst used in the oxidation process (Abdullah *et al.*, 1990).

The solution pH affects surface charge property of $TiO_2$, charge of organic molecule, adsorption of organic molecule on to $TiO_2$ surface and hydroxyl radical concentration. As these properties are pH dependent, pH plays an important role in the photocatalytic degradation of ACN. The effect of pH on the photocatalytic degradation of ACN was studied using initial concentration of 200 ppm and optimum value of catalyst loading (0.1 g/l). The initial pH of solution was varied from 3 to 9. The effect of pH on the reaction rate of ACN is shown in Fig.4. As can be seen from this figure, the maximum degradation of ACN occurs at pH=9. It means that slightly alkaline condition is appropriate for ACN degradation.

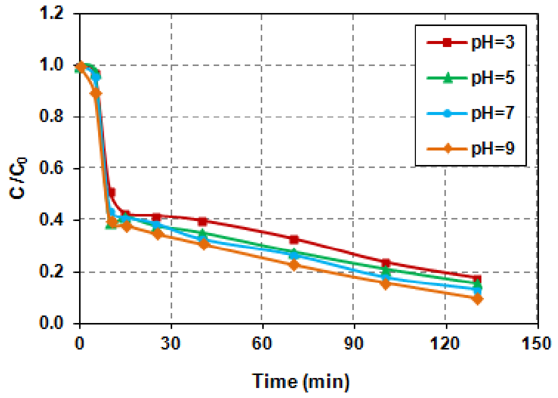

**Fig. 4.** Effect of solution pH on the photo catalytic degradation of ACN.

## Conclusions

In this experimental work, photocatalytic decomposition of ACN using nano $TiO_2$ was investigated in a slurry batch reactor. The results of experiments showed that optimum $TiO_2$ loading, which provides enough surface area for reaction without irradiation loss due to scattering of UV light, was about 0.1g/l. The highest photodegradation rate was obtained in slightly alkaline condition rather than acidic or neutral condition. In addition, photocatalytic degradation of ACN can be simulated by using pseudo-first order reaction rate expression. Furthermore, the effects of inorganic salts were studied. The results revealed that carbonate and bicarbonate ions act as hydroxyl radical scavengers and absorb UV light which results in decreasing degradation rate of ACN. Finally, it can be concluded that UV/$TiO_2$ process can be used successfully for the treatment of ACN containing wastewater.

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