

A Photocatalytic Method for the Degradation of Pyrrolidine in Water

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ABSTRACT: A method for the degradation of pyrrolidine in water is described. The method relies on the photocatalytic degradation of pyrrolidine to CO_2 and NH_3 by UV irradiation and using titanium dioxide semiconductor as a photocatalyst. Compared with direct photolysis, the semiconductor catalytic photolysis gave consistently higher degradation yields for pyrrolidine in water. The effects of variable parameters such as pH, amount of semiconductor and time of photolysis on degradation of pyrrolidine were investigated. An optimal value of pH = 9, amount of semiconductor, 4 mmol.L^{-1} and time of UV irradiation, 25 min. was found. Amount of pyrrolidine was measured spectrophotometrically at $\lambda = 480 \text{ nm}$ using 1,2-naphthoquinone-4-sulphonate as a selective reagent. The concentration of ammonia produced during the reaction was monitored spectrophotometrically at $\lambda = 410 \text{ nm}$ by Nessler's reagent.

KEY WORDS: Pyrrolidine, Photocatalytic, Degradation, Photolysis, Semiconductor catalysis

INTRODUCTION

Pyrrolidine and other structurally related amines are used as intermediates in manufacturing of rubber chemicals; curing of epoxy resins, and in organic synthesis. These compounds are produced annually in very large amounts and employed in a wide range of applications [1-4]. Its presence in the environment is a cause for concern due to its ready conversion to carcinogenic N-nitrosopyrrolidine [5-7].

The microbial decomposition of nitrogenous compounds containing a five member saturated ring system has been investigated by several workers. A path-

way for the utilization of pyrrolidine by *Pseudomonas fluorescens* has been proposed by *Jakoby* and *Fredericks* [8] which involves a dehydrogenation and hydration leading to γ -aminobutyric acid (GABA). Pyrrolidine biodegradation in biological effluent treatment plants is widely regarded a problem. Despite a simple structure it is relatively recalcitrant to biodegradation. One reason for its apparent resistance to biodegradation may be the fact that only organisms reported to degrade it as a sole carbon and energy source are incapable of rapid growth and only

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occur in the environment in small amounts [9].

Environmental applications of semiconductor photocatalysis has grown exponentially. In the areas of water, air, and wastewater treatment, the rate of publication exceeds 200 papers per year over the last 10 years [10].

In view of the resistance of pyrrolidine to biodegradation it was thought desirable to study its photocatalytic degradation. The photocatalytic process utilizes UV or visible irradiation of an aerated water containing titanium dioxide catalyst. This method suggests a complete degradation of pyrrolidine to carbon dioxide and ammonia.

MATERIALS AND METHODS

Pyrrolidine and all chemicals were obtained from Aldrich chemical company Ltd. and solutions were prepared in double distilled water. The anatase form of TiO_2 particles employed in this study were supplied from Merck with purity greater than 99.9%.

Shimadzu-160 UV-Vis spectrophotometer, Metrohm-620 pH meter and thermostate bath HAAKE model F122 were used.

The photoreactor used in this study which is shown in Fig. 1, contained a 400 W high pressure mercury lamp or 150 W visible lights, two beakers (2 L) equipped with magnetic stirrers connected to a thermostat bath and a fan to cool the lamps [11]. Batch reactors consisted of cylindrical Pyrex tube (15 cm, 2cm i.d.). The pyrrolidine solutions was added to the reactor along with a predetermined amount of TiO_2 particles. The solution pH were maintained constant at the desired levels with NaOH and H_2SO_4 solutions and were monitored and adjusted continuously during the course of the reaction. The dissolved oxygen levels of the reaction solutions were maintained constant by the oxygen flow rate of $6 \text{ mL}\cdot\text{min}^{-1}$ at 1 atm. An aliquot of solution was then sampled for absorbance measurement. After the light source was turned on, a small portion of reaction solution was withdrawn in an intermittent periods of time and centrifuged to remove TiO_2 at 500 rpm for 10 min, then analyzed for pyrrolidine and ammonia concentrations. The concentration of pyrrolidine as determined by an adaptation [12] of the method of

Stevens & Skov [13]. This method involves the coupling of secondary amines to sodium 1,2-naphthoquinone-4-sulphonate to produce an orange colour. This colour can be assayed spectrophotometrically by measuring its absorbance at 480 nm against a reagent blank. Standard solutions containing between 0.1 and 1μ moles of pyrrolidine, was made up to 10 mL total volume in buffer (KH_2PO_4 , $2 \text{ g}\cdot\text{L}^{-1}$; pH=7.0). To this was added 0.04 mL of a 3% w/v sodium 1,2-naphthoquinone-4-sulphonic acid solution, immediately followed by 0.1 mL of 1 M NaOH. The sample was mixed thoroughly. After 20 min, the absorbance was read at 480 nm in a spectrophotometer, against a similarly treated reagent blank. Ammonia was estimated using *Nessler's* reagent, the resulting yellow colour was measured at 410 nm against a reagent blank similarly treated.

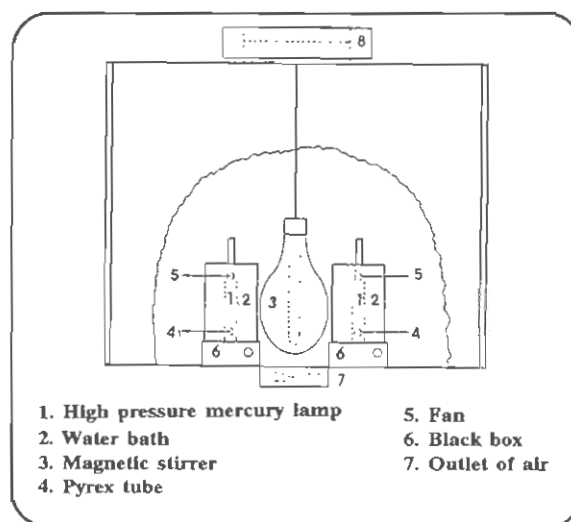


Fig. 1: Schematic diagram of the photoreactor

Typically, a reaction run involved the addition of 0.1 mmol of TiO_2 to 25 mL of $125 \text{ mg}\cdot\text{L}^{-1}$ solution of pyrrolidine in double distilled water. The solution was then saturated with oxygen by bubbling with flow rate of $6 \text{ mL}\cdot\text{min}^{-1}$ and irradiated with UV or visible light for the desired time.

RESULTS AND DISCUSSION

Photocatalysis of pyrrolidine using UV irradiation and oxygen.

Fig. 2 shows the percent loss of pyrrolidine vs

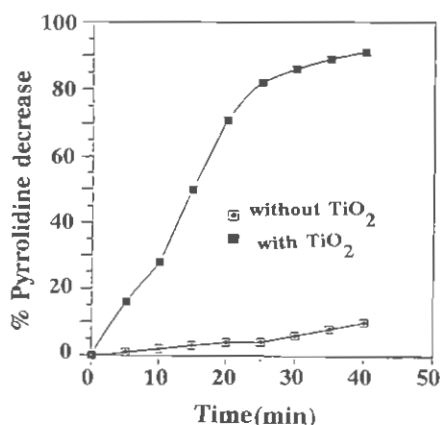


Fig. 2: Percent of pyrrolidine degraded vs time using 0.4 mmol.L^{-1} TiO_2 (or without TiO_2), oxygen with flow rate of 6 mL. min^{-1} and UV irradiation

time for two different experiments:

a) in the presence of TiO_2 , and b) in the absence of TiO_2 .

In the presence of TiO_2 , degradation of pyrrolidine was rapid and completed after 25 min, but in direct photolysis in the absence of TiO_2 , degradation was negligible. The amount of ammonia produced in photocatalytic degradation of pyrrolidine was almost the same as the degraded amine.

pH effect on the decomposition rate of pyrrolidine.

A series of experiments were carried out at pH 5-11 to study the effect of pH on degradation of pyrrolidine. These results revealed that the degradation of pyrrolidine increased from pH 5 to 9 then remained constant for pH 9 to 11 (Fig.3).

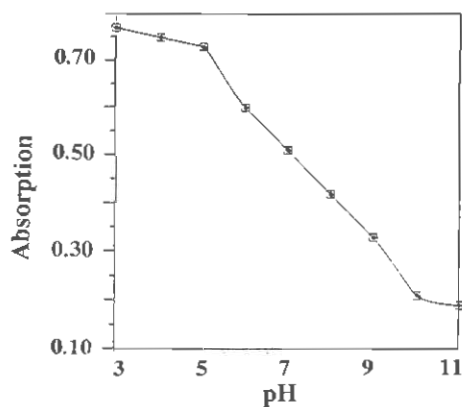


Fig. 3: Effect of pH on the degradation of pyrrolidine.

Effect of TiO_2 concentration on the degradation of pyrrolidine

A series of experiments were carried out with different concentration of TiO_2 from 1 to 40 mmol.L^{-1} . The results indicated that the optimum concentration of TiO_2 for degradation efficiency of pyrrolidine was 4 mmol.L^{-1} (Fig.4).

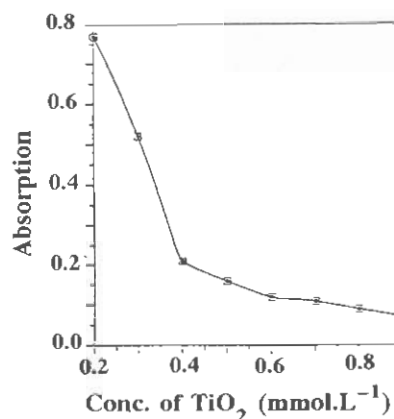


Fig. 4: Effect of TiO_2 concentration on degradation of pyrrolidine

CONCLUSIONS

The photocatalytic degradation process with TiO_2 particles has been shown in this study to be feasible for achieving high degrees of pyrrolidine removal. Almost complete disappearance was observed in only a few minutes of illumination time. The higher removals at basic conditions were possibly attributed to the increased amounts of undissociated pyrrolidine species adsorbed on the TiO_2 surface. It is suggested that the degradation is occurring via hydroxyl radical since the oxidation from pH 5 to 11, becomes more and more effective.

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