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The photocatalytic degradation of atrazine on nanoparticulate TiO_2 films

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Abstract

The photocatalytic removal of atrazine from water was investigated using immobilised TiO_2 films in a stirred tank reactor designed to maximise mass transfer. The degradation of atrazine was demonstrated with a number of breakdown products identified including the stable end product cyanuric acid. The process was monitored using high performance liquid chromatography (HPLC), total organic carbon analysis (TOC) and liquid chromatography–mass spectrometry (LC–MS). A decrease in the TOC was observed and attributed to the oxidative degradation of atrazine side chains. Intermediates identified included 2-chloro-4-acetamido-6-isopropylamino-1,3,5-triazine, 2-chloro-4-ethylamino-6-(1-methyl-1-ethanol)amino-1,3,5-triazine, 2-chloro-4-ethylamino-6-(2-propanol)amino-1,3,5-triazine, 2-hydroxyatrazine, desethylatrazine, deisopropylatrazine, 2-hydroxydesethyl atrazine and cyanuric acid. Operational parameters such as catalyst loading, oxygen concentration, initial pollutant concentration and UV source were investigated. Atrazine removal followed first order kinetics and the rate was dependent upon catalyst loading up to an optimum loading (above which a decrease in the degradation rate was observed). No difference in the rate was observed when either air and O_2 sparging was used. The rate was directly proportional to initial concentration in the range studied. The use of UVB irradiation did not appear to increase the rate of degradation in comparison with UVA irradiation. However, the maximum apparent quantum yield for the photocatalytic degradation was higher under UVB (0.59%) compared to UVA (0.34%).

Keywords: Atrazine; Photocatalysis; Titanium dioxide; Water treatment

1. Introduction

Persistant organic pollutants (POPs) have been identified as an increasing problem in our drinking water supplies [1]. Such substances can enter the water supply from various sources and are not effectively removed by conventional water treatment processes [2]. Pesticides have been classed as POPs due to their resistance to natural degradation processes, and hence ability to remain in the environment for long periods of time. By their very nature they are designed to be toxic and kill unwanted organisms. They act by interfering with the biochemical and physiological processes that are common to a wide range of living systems, e.g. parathion used for the control of insects on crops, affects the central nervous system and the liver, whereas atrazine used for the control of broad leaf and grassy weeds, inhibits photosynthesis. Although these compounds are designed to be organism specific they can attack non-target organisms and as a result, cause serious environmental damage. Atrazine {2-chloro-4-ethyl-amino-6-isopropylamino-1,3,5-triazine} is one of the most common pesticides found in ground water sources and drinking water supplies. In some countries restrictions on its use have been implemented, while in others, bans have even been imposed. Atrazine has been detected above the recommended levels (0.1 ppb or $\mu g\,dm^{-3}$) throughout Europe [3–5] and the United States [6,7] and is considered as a priority substance by the EC [8]. It is characterised by its high persistence and lifetime of days up to years in the environment [9,10]. Its persistence is due to the stability of the *s*-triazine ring, which inhibits natural degradation. Atrazine has also been reported to have endocrine disrupting capabilities [11,12].

Semiconductor photocatalysis is a possible alternative/complimentary technology for the treatment and purification of polluted water [13–16]. The process utilises a combination of UV light and a semiconductor catalyst and is capable of degrading chemical pollutants by both oxidative and reductive pathways. Titanium dioxide (TiO_2) is the photocatalyst of choice for water treatment investigations because it is non-soluble under normal pH ranges, it is photoactive, photostable, with *Degussa*

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P25 being widely used as the research standard in the field of photocatalysis.

Photocatalysis has been reported to be effective in the degradation of a wide range of pesticides including the triazine herbicides [17], with TiO_2 being the most widely employed photocatalyst for pesticide destruction in water for research studies [18]. Out of all pesticides reported the triazine herbicides are the only group resistant to total mineralisation. So far techniques such as ozonation and removal by adsorption onto activated carbon have been considered to help eliminate atrazine from the environment [19], however it still remains a threat within the environment.

Many workers have studied the photocatalytic degradation of the triazine herbicides, in particular atrazine [19–23]. Hustert et al. [21] studied the photocatalytic treatment of the triazine herbicides, atrazine, simazine, and cyanazine. They reported that the degradation of the triazines occurred by several steps leading to a final stable product, cyanuric acid, and complete mineralisation of atrazine was not observed. It has been reported by others that full mineralisation of the *s*-triazine herbicides does not occur, with cyanuric acid being produced as the final product of degradation, with prolonged photocatalytic treatment required [23]. However, a recent paper has reported the successful degradation of cyanuric acid by the addition of fluoride ions to a TiO_2 suspension [24].

Photocatalytic degradation under solar irradiation has been reported to be effective for the photocatalytic degradation of *s*-triazines [20,22]. Konstantinou et al. [22] investigated the photocatalytic treatment of *s*-triazine herbicides and organophosphates insecticides using a TiO_2 suspension irradiated under simulated solar light. They reported half-lives ranging from 10.8 to 38.3 min for the *s*-triazines under their reactor conditions, but complete mineralisation again was not observed. Minero et al. [20] investigated the photolytic and photocatalytic degradation of atrazine in a large-scale solar reactor. They reported that atrazine was degraded by photolysis alone (in the absence of photocatalyst), but there was no reduction in the TOC. However, with TiO_2 photocatalyst present, the rate of degradation increased over that observed with photolysis and a reduction in the TOC was observed. However, complete mineralisation to CO_2 was not observed and the reduction in the TOC corresponded to the oxidation of the lateral side chains with only five of the eight carbons of atrazine removed.

Hequet et al. [19] investigated the photolytic and photocatalytic degradation of atrazine and reported efficient UV photolysis with $t_{1/2} < 5$ min and hydroxyatrazine generated as the main intermediate. Cyanuric acid was reported as the final end product. In contrast, under photocatalysis, atrazine was found to have a $t_{1/2} \sim 20$ min, with desalkylated compounds as the major intermediates, with final degradation to cyanuric acid. Therefore the photocatalytic degradation followed the pathway involving oxidation of the lateral side chains rather than the hydroxylation pathway as seen with photolysis. The half-lives reported for the photolysis and photocatalysts cannot be directly compared, as the wavelengths and intensity of the radiation differ in both cases. The majority of research carried out has involved suspensions of TiO_2 though a few studies have been conducted on immobilised films [25–30]. A list of identified intermediates and their abbreviations reported in literature for the photodegradation of atrazine are given in Table 1.

Table 1
Compound names and abbreviation for atrazine and intermediate photodegradation products

Abbreviation	Compound
Atrazine	2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine
AOHE	2-Chloro-4-acetamido-6-isopropylamino-1,3,5-triazine
AOHI1	2-Chloro-4-ethylamino-6-(1-methyl-1-ethanol)amino-1,3,5-triazine
AOHI2	2-Chloro-4-ethylamino-6-(2-propanol)amino-1,3,5-triazine
OHA	2-Hydroxyatrazine
DEA	Desethylatrazine
DIA	Deisopropylatrazine
DAA	Desethyldesisopropyl atrazine
OHDEA	2-Hydroxydesethyl atrazine
OHDIA	2-Hydroxydesisopropyl atrazine
$ClOHNH_2$	2-Chloro-4-amino-6-hydroxy-1,3,5-triazine
$Cl(OH)_2$	2-Chloro-4-hydroxy-6-hydroxy-1,3,5-triazine
OHOHIDEA	2-Hydroxy-4-amino-6-(1-methyl-1-ethanol)amino-1,3,5-triazine
OHOEDIA	2-Hydroxy-4-acetamido-6-amino-1,3,5-triazine
AME	2-Hydroxy-4,6-diamino-1,3,5-triazine
ADE	2,4-Dihydroxy-6-amino-1,3,5-triazine
CYA	2,4,6-Trihydroxy-1,3,5-triazine

The photocatalyst may be used either in the slurry or immobilised form. Using an immobilised system one can obtain a configuration in which all the catalyst is illuminated and further eliminates the need for post treatment catalyst recovery. A disadvantage with an immobilised system is that mass transfer limitations can reduce reactor efficiency and/or interfere with the measurement of true degradation kinetics. This paper reports on the photocatalytic degradation of atrazine on immobilised TiO_2 films in a stirred tank reactor which has been specifically designed to maximise mixing and mass transfer and thus give more accurate measurement of intrinsic degradation kinetics.

2. Materials and methods

2.1. Immobilisation of TiO_2

TiO_2 (*Degussa P25*) was immobilised onto indium doped tin oxide coated borosilicate glass (Donnelley Co-Operation USA) using an electrophoretic deposition technique [31] by applying a fixed negative potential of 25 V to the conducting glass for a set period of time. The TiO_2–ITO glass was then annealed in air at 673 K for 1 h to effect particle adhesion and cohesion. Gravimetric analysis was used to determine the TiO_2 loading.

2.2. Photocatalytic reactor

A custom built stirred tank photo-reactor (STR) previously reported [32], was used to study the photocatalytic degradation of atrazine in water. The system consisted of a water-jacketed walled vessel creating a reservoir and a stainless steel propeller used to create a turbulent flow within. Good mass transfer