

Photo -Chemical Degradation of 2, 4- Dichlorophenoxyacetic acid (2, 4-D) in the Effluent

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Abstract

Background: 2, 4-dichlorophenoxy acetic acid (2, 4-D) is well known as inexpensive herbicides but it can give rise to undesirable pollution. The objective of this investigation was to describe a photo-chemical system for degradation of 2, 4-D.

Methods: A designed photolytic cell system was used in this study with a 150W or 400W UV lamp. A set of experiments was carried out at pH 1.5, 2.5, 3.5 and 4.5 to investigate the effect of pH on the degradation rate of 2, 4-D. The samples were collected and analyzed by UV spectrophotometer, and HPLC.

Results: With a 150 WUV- source, the percentage degradation of 2, 4 -D after one hour was 3% while 60% of destruction was achieved using a 400W. The percentage degradation of 2, 4-D was 19% and 99.9% after 8 hours with a 150 W or 400 W UV lamp, respectively. The complete degradation of 2, 4-D was achievable with addition of hydrogen peroxide after 120 and 15 min using 150 W and 400 W UV lamp, respectively.

Conclusion: This investigation finding shows that 2, 4-D is degradable in acidic pH of 2.5 or 3.5. In addition, 2, 4-D degradation can be achieved in wastewater by UV light and depends on intensity of lamp or present of H₂O₂ oxidant.

Keyword: 2, 4-D, Photo--chemical degradation, UV radiation, effluent

Introduction

Removal of pollutants in drinking water and effluent may involve techniques such as flocculation, filtration, and adsorption procedures. One of the traditional purification methods involves activated carbon filtration. However, this technique only removes the pollutants and does not destroy them. Biodegradation is an important water treatment method, but microorganisms leave intact many persistent organic contaminants.

2, 4-D was rapidly degraded in sunlight under laboratory conditions, but photo degradation has not been demonstrated in the field (1). Johnson et al. (2, 3) reported that 2, 4-D degradation rates in soils remained relatively constant with

and without sunlight, suggesting that photo degradation was not an important process in the field. They found also that soil organic content and soil pH were the main determinants of 2, 4-D adsorption in soils.

Microbial degradation of 2, 4-D can take place in bottom sediments if the appropriate microbial population is present and the pH level is sufficiently high, but it is not likely to occur in the water column (4). There are conflicting reports as to whether microbial degradation occurs in aquatic systems (5-7). Degradation rates are determined by the microbial population, environmental pH, soil moisture, and temperature (5, 8).

Johnson et al. (9) found that soil organic content and soil pH was the main determinants of

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2, 4-D adsorption in soils. Adsorption increases with increasing soil organic content and decreasing soil pH (2, 9). Alan et al. investigated the efficacy of adsorbents for 2, 4-D removal from water environment (10).

Chemical decomposition is the degradation of an herbicide to one or more of its components via chemical reactions. 2, 4-D is relatively persistent in the environment, and does not readily undergo chemical degradation, relative to other herbicides (5).

Oturan described (11) an indirect electrochemical method for ecological treatment of water contaminated by organic pollutants and 2, 4-D as well.

The World Health Organization (12) concluded that 2, 4-D does not accumulate or persist in the environment. The primary degradation mechanism is microbial metabolism, but mineralization and possibly photolysis may also play a role. The type of 2, 4-D formulation applied does not significantly affect the rate of degradation (8, 9).

2, 4-D is considered of moderate toxicity to animals, although LD₅₀ levels vary significantly between formulations and animal species (13). 2, 4-D can bio-accumulate in animals. In Russia, residues of more than ten times the allowable level were found in eggs, milk, and meat products served by public caterers and one study reported residues in 46% of tested cattle (5). Risk to browsing wildlife, however, is low; (13) analyzed 2, 4-D residues in forest browse following aerial application to forests in Oregon and found them to be below the concentrations known to cause effects in mammals. 2, 4-D can accumulate in fish exposed to concentrations as low as 0.05 ppm (14). 2, 4-D can be absorbed through the skin or through the lungs if inhaled. Applicators of 2, 4-D, particularly those using back-pack sprayers, are at the greatest risk of exposure (13, 15). Once in the body, 2, 4-D is distributed rapidly with the greatest concentrations appearing in the kidneys and liver (15).

The generalized use of pesticides and herbicides and their persistence in the aqueous environment (16) has led to the need of finding effective methods of destroying them. Water can be polluted by various ways including run off from crop land, and effluent from industry.

The aim of this study was to describe a photolytic system for degradation of 2, 4-D to achieve effluent clean up.

Materials and Methods

The photolytic cell system used in this investigation (Fig. 1) consists of UV probe (A) surrounded by a reaction Chamber (B) of 3.5 dm³ capacity through which the fluid to be treated is pumped from a reservoir (c) via an inlet (D) and back to the reservoir via outlet (E). The fluid flow rate (10 dm³ min⁻¹) was controlled by valve 1. Compressed air is used as the oxidant in the photolysis and is supplied through inlet (F) and exit through (G). The temperature in the system was measured by a digital thermocouple probe (H). The temperature in the reaction chamber is maintained at 23-30 °C by passing water through a cooling jacket (I) surrounding the UV probe.

A set of experiments was carried out at pH 1.5, 2.5, 3.5 and 4.5 to investigate the effect of pH on the degradation rate of 2, 4-D. Next experiments were carried out to investigate the effect of 150 and 400 W UV- sources on the degradation of 2, 4 -D using a photolytic system at pH 3.5. Also a set of experiments was done to investigate the effects of UV irradiation source in the presence of H₂O₂. The samples were collected each hour and analyzed using a Unicam UV/Vis spectrophotometer at 282 nm and also by reverse-phase chromatography using a Waters HPLC system, equipped with a u.v. detector set at 280 nm and fitted with a reverse phase Hypersil ODS 5 lm, 4: 6mm- 25 cm column from Supelco Inc.

Results

The natural pH of the model solution containing 50-mg dm^{-3} of 2, 4- D was 3.5. The results showed that, although the initial degradation rate increased by decreasing the pH from 3.5 to 2.5 but no further advantage was achieved by decreasing pH to 1.5. Increasing pH from 3.5 to 4.5 resulted in a small decrease in the initial rate of degradation but the same level of degradation (99.9%) was achieved after 8 hours at all pH values studied in this work. All subsequent studies were carried out at pH 3.5.

The results show that with a 150 W UV- source the percentage degradation of 2, 4 -D after one hour is only 3% while 60 % of destruction is achieved using a 400W. The corresponding values after 8 hours are 19 and 99.9%, respectively (Fig. 2a). The addition of hydrogen peroxide ($5\text{cm}^3\text{dm}^{-3}$), as an oxidant, increases the degradation rate of 2, 4-D and complete mineralization is achieved after 120 and 15 minutes using 150 W and 400W UV- lamp, respectively (Fig. 2b). These results confirmed that the addition of an oxidant is necessary to achieve degradation when a low intensity UV-lamp is used.

The photolytic degradation of organic species proceeds through the formation of different in-

termediates. The finding results show that much higher concentrations of these two intermediates are achieved in the case of 150 W UV lamp compare to 400 W. HPLC chromatograms (detection at 280 nm) for determination of 2,4-D is shown in Fig. 3.

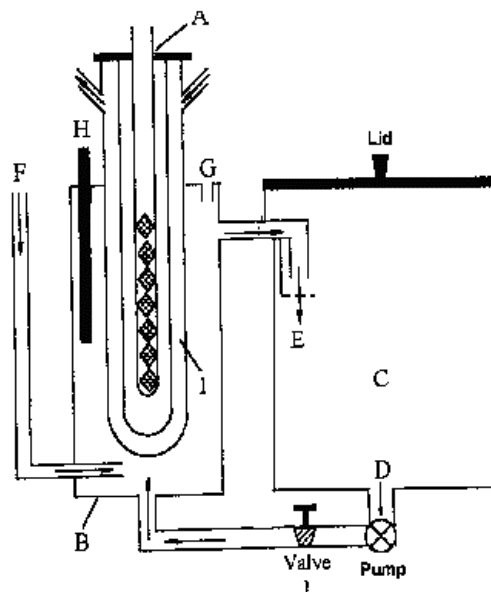


Fig. 1: The photolytic cell system was used

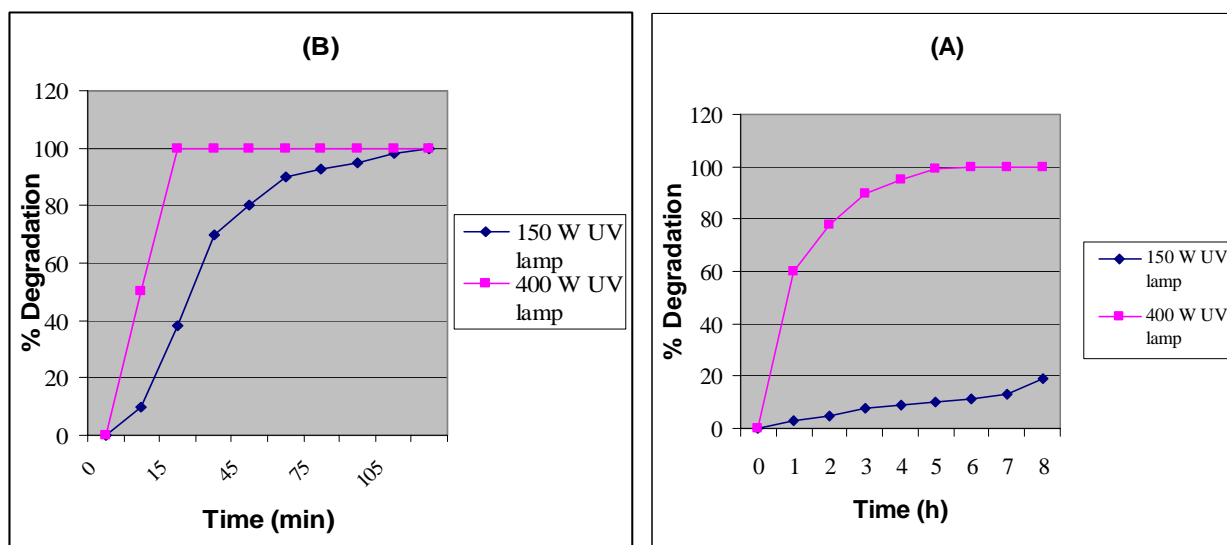


Fig. 2: Effect of UV irradiation source on the degradation of 2, 4-D A) in the absence and B) in the presence of H₂O₂

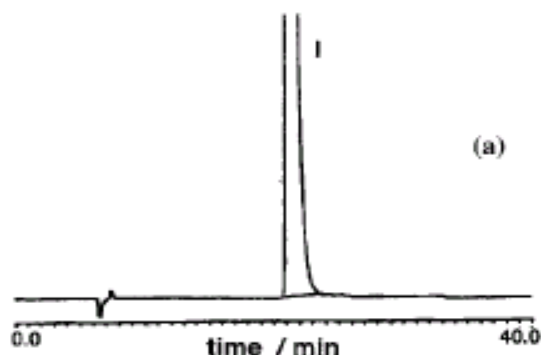


Fig. 3: HPLC chromatograms (detection at 280 nm) for determination of 2, 4-D

Discussion

2, 4-D has a moderate toxicity for animal (13) and also can bio-accumulate in animal (5, 14). Therefore, human can take 2, 4-D from feed-chain, air and water.

These findings show that 2, 4-D is degradable in acidic pH of 2.5 or 3.5. 2, 4-D will change form and function with changing in water pH (5). In alkaline (pH > 7) waters, 2, 4-D takes an ionized (negatively charged) form that is water-soluble and remains in the water column. Theoretically, in water of a lower pH, 2, 4-D will remain in a neutral molecular form, increasing its potential for adsorption to organic particles in water, and increasing its persistence (14).

This study showed that 2, 4-D degradation could be achieved in wastewater by UV light and it depended on intensity of lamp or present of H₂O₂ oxidant. The influence of various reaction parameters on herbicide 2, 4-dichlorophenoxyacetic acid (2, 4-D) removal were examined by Lee Y. et al (17) and also by Trillas M. (18) et al. but they used catalyzed.

Paterlin et al. Investigated photo degradation of 2, 4-D and showed that under optimized conditions, 20 min was sufficient to mineralize 93% of TOC from 2, 4-D (19).

Although microbial degradation process is an option for organic pollutant in the water but there are conflicting reports as to whether mi-

crobial degradation occurs in aquatic systems (5- 7).

The results of this study show that photo-chemical method is rapid compared with biological method and also are environmentally friendly.

Acknowledgements

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