Photochemical Treatment of Herbicide/Pathogen Contaminated Agricultural Water in the Rio Grande Basin

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The paper describes the photochemical treatment of chemical (herbicide) and biological (pathogens) contaminants in agricultural water. We investigated the photolysis of dissolved herbicide atrazine and photocatalytic sterilization of pathogen E-coli, common in the Rio Grande valley agricultural run-off water and rivers. Atrazine ($C_8H_{14}ClN_5$), a widely-used herbicide used in the cane and corn fields, can cause prostate cancer, cardiovascular damage, muscle and adrenal degeneration, and congestion of heart, lungs, and kidneys. It also causes sexual deformities in endangered species (e.g., Leopard frogs) [1-3]. Without treatment, the atrazine-contaminated water is hazardous and detrimental to water sustainability in the Rio Grande Basin.

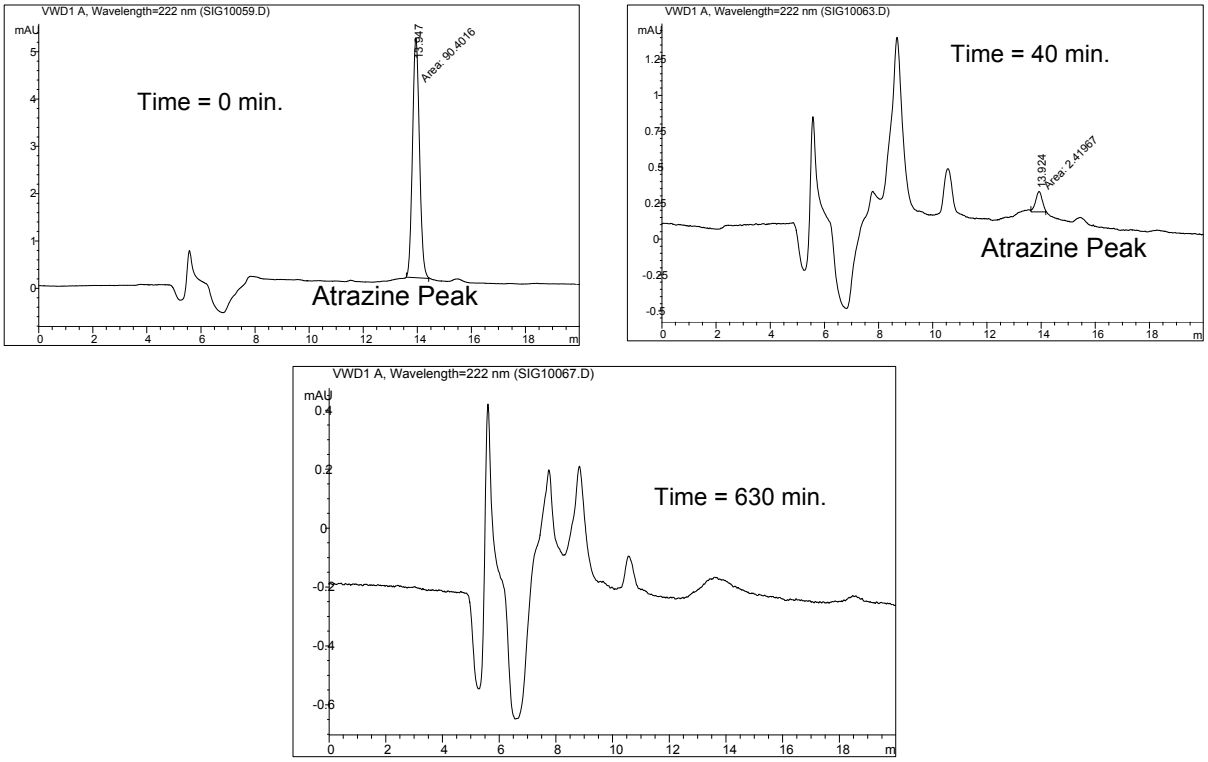

Fig. 1 Photolysis of Atrazine in Water monitored with Agilent 1100 HPLC

Generally speaking, the photochemical treatment includes photolysis using UVC and photocatalysis using UVA [4-9]. The former directly breaks down chemical bonds or kills pathogens while the latter can use lower energy photon such as UVA or visible light over a photocatalyst to generate electron-hole pairs and free radicals. In our lab, atrazine rapidly decomposes from 40 ppb to below 3 ppb in 23 minutes under UVC (3.0 W) irradiation. The photolysis results in two major and two minor byproducts that can further decompose to CO_2

and water, Fig. 1. Hydroxyatrazine consists of up to 77% of decomposed atrazine, and is relatively harmless compared to atrazine. The kinetic data of the photochemical decomposition of atrazine can be fitted very well with a first-order rate equation:

$$dC/dt = -kC \qquad (1)$$

(Fig. 2, R^2= 0.996). The first-order rate equation states that under a constant UVC irradiation, the atrazine decomposition rate is proportional to its concentration. hydroxyatrazine photolyzed following the first order rate equation with a much slower rate constant than that of atrazine. Under 3 W UVC irradiation in a 3.5 L reactor, it has a half-life time of 198 min compared with 6.2 min for atrazine photolysis (Fig. 3).

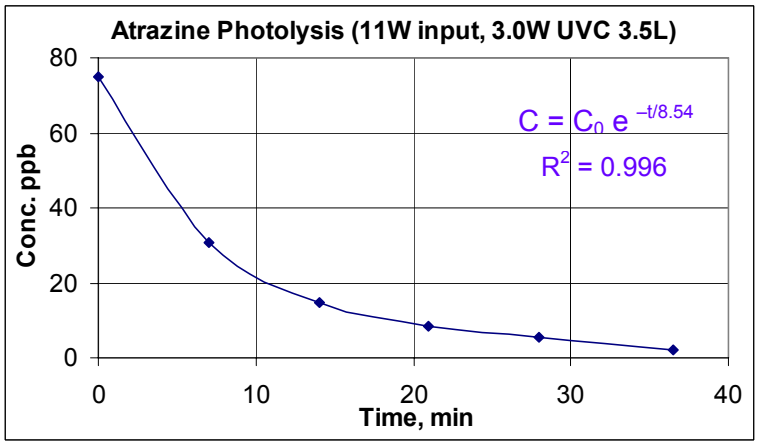

Fig.2 Atrazine photolysis follows a first-order rate law.

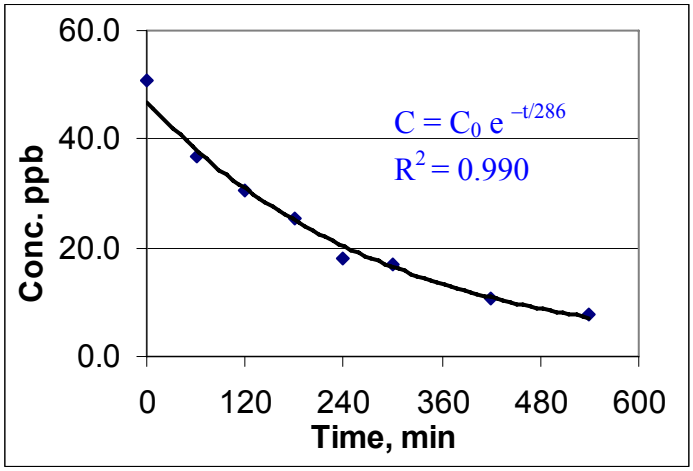

Fig. 3. Hydroxyatrazine photolysis follows a first-order rater law.

At the same concentration, the atrazine decomposition rate is proportional to the UVC output squared (Fig. 4):

$$k = 0.0129\ P^2 \qquad (2)$$

where P is the UVC output

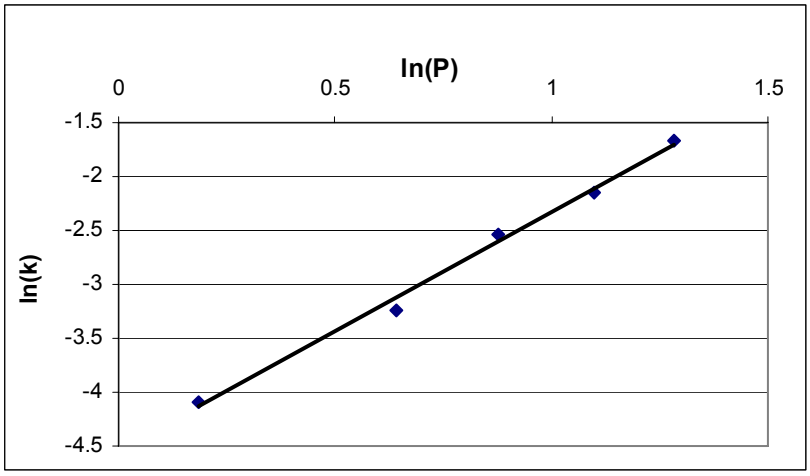

Fig.4 The first-order rate constant is proportional to the second power of the UVC light output.

At the same UVC input, the atrazine decomposition rate is proportional to the reactor volume (Fig. 5). Basically, all the reactors are geometrically similar, as the ratio of used height to the reactor diameter is very close.

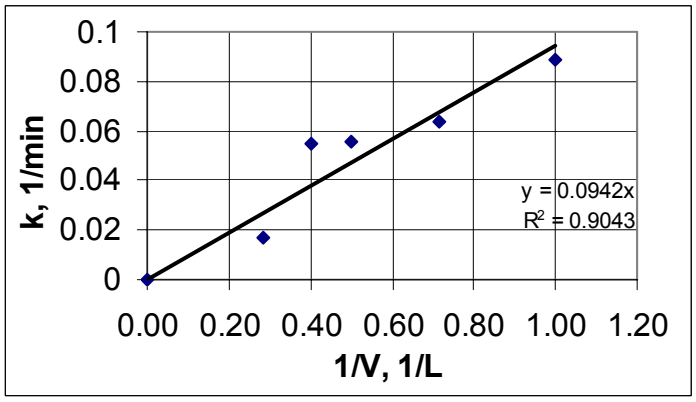

Fig. 5. Rate constant and the reactor volume under 1.2W UVC irradiation.

In the practical conditions, drinking water transmittance can vary from 0.65 to 0.98 [10]. Water transmittance reduction will decrease the UV quanta that reach the reactants far from the lamp. Parts of UV adsorption result from impurities, while UV absorption by atrazine is necessary for the photodecomposition. Notice that 60 ppbm atrazine only reduced the transmittance from 0.8375 to 0.8338, as atrazine concentration was very low. So using the transmittance of water sample is a reasonable and practical to adapt to the influence of the water medium (Equ. 3).

$$k = 0.07321\ (TP)^2/V \qquad (3)$$

where V is the reactor volume used, dm^3 and T is the transmittance in 1cm cell.

Overall, we give the kinetics rate equation of atrazine photolysis as the following:

$$dC/dt = -0.07321\ (TP)^2\ C\ /V \qquad (4)$$

Photochemical sterilization of E-coli in our lab showed one order of magnitude decrease (89% reduction) in Colony Forming Units (CFU) when a 4W UVA lamp (1.5 in away) was shined upon a vessel containing Degussa P-25 TiO_2 photocatalyst in 40 minutes. The blank tests showed TiO_2 alone can reduce E. Coli CFU by 80% and UVA alone by 36% in 40 minutes, Figure 6. More experiments on the light intensity effect are needed.

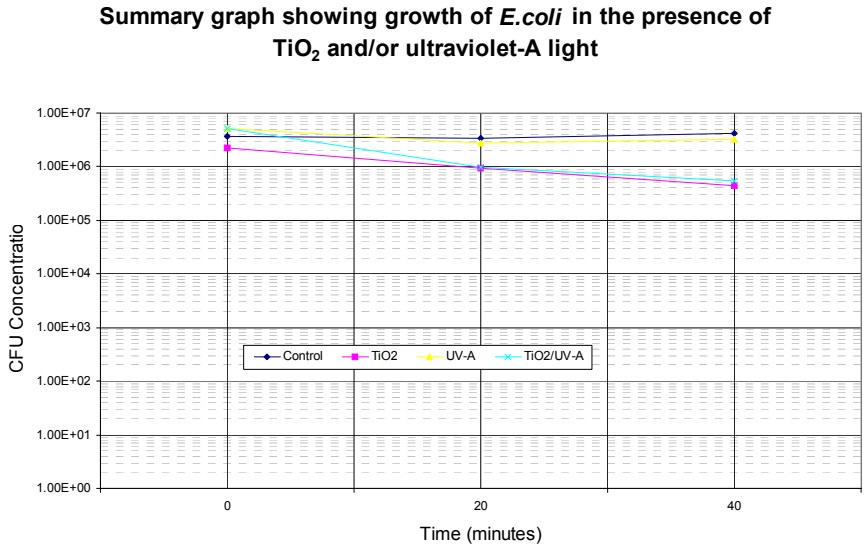

Fig. 6 Photochemical sterilization of E. Coli (UVA + TiO2) vs. blank tests

References

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