

Cataphotolysis of Propanil in Water Using Nanotechnology

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ABSTRACT

Herbicides and pesticides in California agriculture, are considered to pose a significant threat to water contamination by transporting chemicals into surface and ground water. As such, the removal of these water contaminants is critical to ensuring a high quality of water is available for California water resources and to safeguard the environment. We are developing a technique that combines nanotechnology and visible light radiations for the removal of pesticides from water. Propanil has been chosen for investigation in the present research project. We measure the kinetics of the decomposition process for each of the compound by monitoring the decay during the cataphotolysis using the Ultraviolet-Visible (UV-Vis) spectroscopy and/or Fourier transform infrared spectroscopy combined with attenuated total reflectance (FTIR-ATR) techniques. Our preliminary data indicate that Propanil in water undergoes cataphotolysis with visible light in the presence of nanomaterials. It is also found that the cataphotolysis of the Propanil molecule in water follows the first order chemical kinetics, and the cataphotolysis of Propanil was faster under the sunlight radiation than the light bulb radiation.

Keywords: nanotechnology, cataphotolysis, water

1 INTRODUCTION

Irrigation of farmland consumed approximately 80% of total water usage in California. The costs associated with groundwater monitoring and cleansing have cost the state more than \$33 millions of dollars. This research project has significant economic impact to the California agricultural industry and consumers by helping clean up surface and ground water contaminated by pesticides. Contamination of California ground and surface water by pesticides, including herbicides and fungicides, due to agricultural application is an important environmental issue that affects California welfare. It has been reported that a total of 195 million pounds and 189 million pounds of pesticides were used for

agricultural practice in California in 2013 and 2014, respectively [1], among them Propanil is in the top 100 pesticides used list [1]. Because pesticides are relatively mobile and persistent in soil they can penetrate into ground water following their soil application by farmers. As a result, pesticides have been detected in surface and ground water in many areas of California with various concentrations [2-10]. Crops including vegetables and fruit could be contaminated if the water containing pesticides is reused for irrigation. Research shows that consumption of well water contaminated with pesticides may play a role in the etiology of Parkinson's Disease in Rural California [11-12]. It is important to remove pesticides from the irrigated water prior to its reuse.

There are several techniques currently used for water organic contaminants removal, including Activated Carbon Adsorption [13], Chlorination [14-17], UV Photolysis [18-20], Ozonation [17, 21-23], Ferrate Oxidation [24-25], and UV radiation in the presence of nano-materials [26]. Although these techniques are useful in treating contaminated water, they have limitations in terms of removal completion, efficiency, rates, and operational costs. In addition, the methods for identification and quantification of both organic contaminants and the reaction products in these water treatments are not well developed. It is therefore necessary to develop new techniques and approaches for the contaminated water treatments aiming at pesticides degradation and removal. We are developing a cataphotolysis technique to allow efficient, low cost degradation of pesticides and other organic contaminants in water, with the degradation process being constantly monitored for both contaminants and products.

2 EXPERIMENTAL

Propanil water samples with concentration at ppm (part per million) level are placed into a beaker containing trace amount of hydrogen peroxide and a glass plate coated with nanoparticles. Figure 1 shows the schematics for the cataphotolysis of Propanil in water. The samples are then exposed to visible light radiations coming from either regular light bulb or the Sun, and the change of the Propanil concentration was monitored using ultraviolet-visible spectroscopy. Cataphotolysis of Propanil molecules takes place at the surface of

nanoparticles, on which the reduction-oxidation reactions occur, leading to oxidative degradation of the Propanil molecules. The Propanil degradation is indicated by the absorbance decrease of the ultraviolet-visible spectrum of Propanil at 248 nm. The product of cataphotolysis is probed using liquid chromatography coupled with mass spectrometry (LC-MS), and the acidity of the water sample was measured using a pH meter. Kinetics information is acquired by monitoring the decay of Propanil as a function of time during its cataphotolysis.

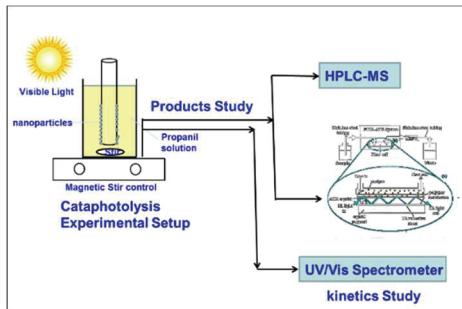
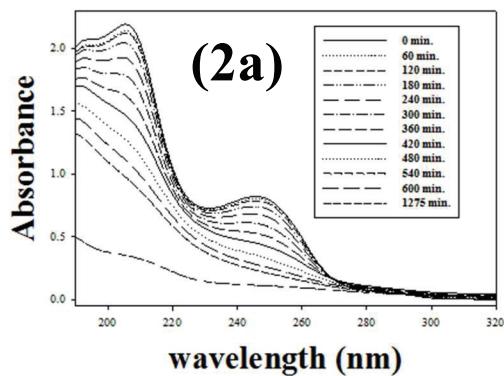


Figure 1: Schematics of experimental arrangement for the nanoparticle and visible light based cataphotolysis experiments.

3 RESULTS

Figures 2-3 show our typical preliminary results of cataphotolysis of 100 mL of 10 ppm Propanil water sample, with Figures 2a and 2b showing the UV spectral decay and the kinetics data collected with the light bulb radiation, and Figures 3a and 3b showing UV spectral decay and kinetic data collected with the sunlight radiation. It can be seen from Figures 2a and 3a that upon exposure to visible light radiation in the presence of the nanomaterials the Propanil in water undergoes cataphotolysis since its characteristic absorption peaks at $\lambda = 248$ nm decrease as irradiation time increases, which results in a decrease of Propanil in the water sample.

100 mL of 10 ppm Propanil + nano-material
light bulb Photocatalysis data



100 mL of 10 ppm Propanil + nano-material
Photocatalysis kinetics data

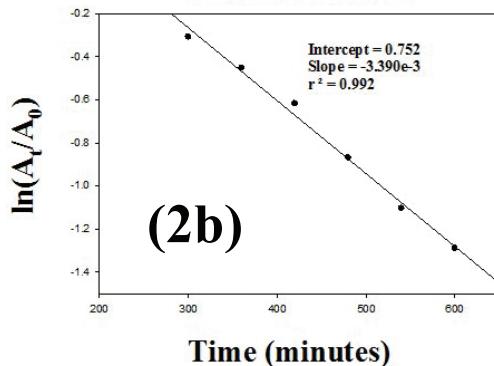
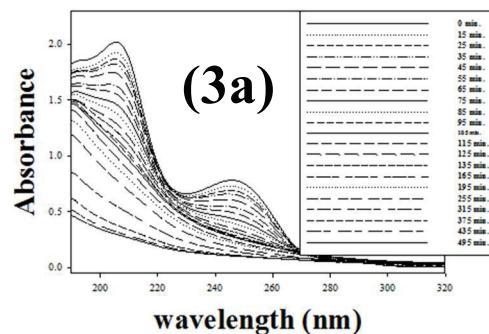


Figure 2. Typical spectral decay (2a) and kinetics (2b) data of visible light cataphotolysis of 100 mL 10 ppm Propanil solution radiated with light bulb.

100 mL of 10 ppm Propanil + nano-material
Sunlight Photocatalysis data



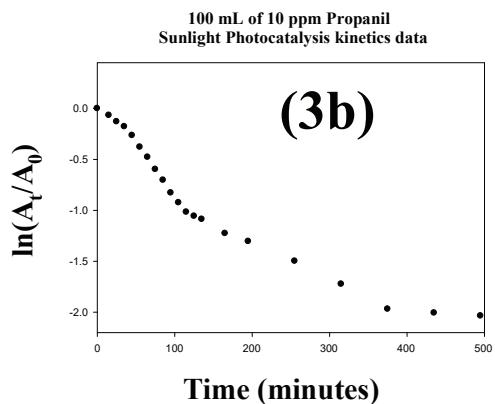


Figure 3. Typical spectral decay (3a) and kinetics (3b) data of visible light cataphotolysis of 100 mL 10 ppm Propanil solution radiated with sunlight.

4 DISCUSSION

Our preliminary results indicate that the technique of nanoparticle and visible light radiation based cataphotolysis can be applied to removal of Propanil from water, and the cataphotolysis of Propanil follows the first order chemical kinetics under light bulb radiation. It is also found that the cataphotolysis takes place faster under the sunlight radiation than under the light bulb radiation, but the sunlight kinetic results suggest a variation of reaction rate with the sunlight intensity variations. However, further study is needed to exclude the influence of the UV radiation for the sunlight radiation experiment in order to confirm that the visible light is responsible for the cataphotolysis.

5 CONCLUSION

Propanil molecules were found to undergo decomposition during cataphotolysis when the water samples are radiated by visible light either from light bulb or from the Sun. The sunlight was found to increase the degradation rate in comparison to the visible light from the light bulb. The cataphotolytic degradation of Propanil in water follows the first order chemical kinetics, with a rate constant of $k = (4.29 \pm 0.49) \times 10^{-3} \text{ s}^{-1}$. No detectable organic products were found from cataphotolysis of Propanil in the LC-MS examination of the water samples. The acidity of the water sample increases, suggesting that the Propanil molecules are oxidized into carbon dioxide, which dissolved in water to form carbonic acid, giving rise to lower pH value than the neutral water.

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